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# Measurement of Volatile Organic Compound Capture Effciency

Radian Corp., Austin, TX

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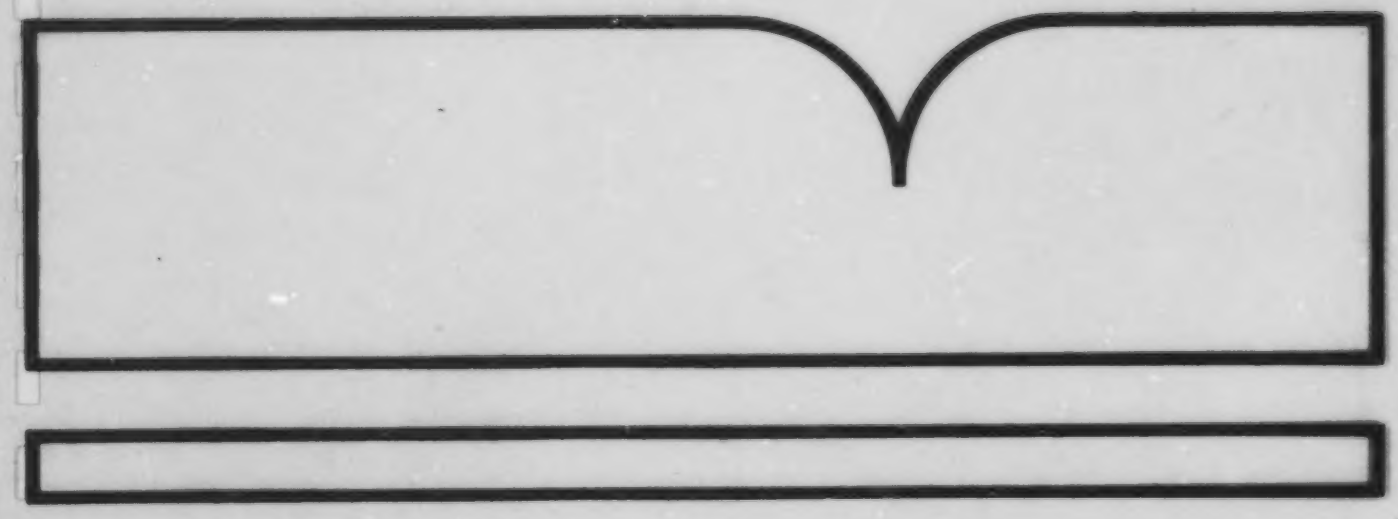

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# MEASUREMENT OF VOLATILE ORGANIC COMPOUND CAPTURE EFFICIENCY

Final Report

by

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16. ABSTRACT

This report reviews the feasibility considerations regarding each of several potential alternate approaches for determining capture efficiency and experimental testing of one approach, the liquid/gas-phase material balance. Two phases of experimental testing were conducted: laboratory and field investigations. The measured mean capture efficiencies for the the field test were higher than expected (106.7% with a coefficient of variation 7.4%). At this time, there is no material balance methodology which is superior to the gas-phase approach using a total enclosure around the regulated coating operation.

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## FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even our health often require that new and increasingly more efficient pollution control methods be used. The Hazardous Waste Engineering Research Laboratory assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Determination of overall emission reduction efficiency and regulatory compliance status of some new surface coating operations requires knowledge of the capture efficiency of emissions. A feasible method for measurement of capture efficiency has been proposed by the U.S. Environmental Protection Agency. It requires total containment of emissions from process lines. In many web coating plants such containment has almost become the norm. The Agency would permit the installation of temporary enclosures for purposes of conducting the performance test. If a method for capture efficiency could be developed which does not require construction of a temporary enclosure, that expense could be eliminated.

This report presents the results of an investigation to identify and evaluate acceptable alternate measurement methods. The results should be of interest to regulatory agencies and industrial sources involved in VOC emissions control. Requests for further information regarding this study should be directed to the project officer at the Hazardous Waste Engineering Research Laboratory, Cincinnati.

David G. Stephan
Director
Hazardous Waste Engineering Research Laboratory
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## ABSTRACT

This research program was initiated with the overall objective of determining an acceptable alternate method for measuring capture efficiency of volatile organic compounds at surface coating operations.

An information search was conducted, and alternate methods were conceptualized and evaluated for feasibility and applicability. The alternate approaches included liquid/gas-phase material balances, use of tracer materials, modeling, and other indirect methods.

Several methods were considered feasible, although the liquid/gas-phase material balance approach was preferred. Therefore, the remainder of the study focused on testing of the liquid/gas-phase material balance method. In the liquid/gas-phase material balance technique, the amount of solvent used at the coater is compared with the measured amount of VOC in the capture stream.

Both laboratory and field tests were conducted to fully evaluate the methodology. Laboratory tests proved encouraging and identified no major problems with the methodology using an EPA Method 25A gas-phase analysis. Laboratory material balance closures averaged 99.9% for pure solvents and 102.2% for solvent and solid blends. However, field capture efficiency test results were unexplainably high. Liquid/gas-phase closures employing Method 25A analyses in the field test averaged 106.7% when determined for 24 hour periods and 103.0% when determined for batch periods.

Capture efficiency determinations by the liquid/gas-phase method at sites with more complex stream configurations or more non-steady state operations are expected to be more variable.

A comparative evaluation of the alternatives considered and the existing gas-phase enclosure method concluded that there is not a readily available alternate method that will produce equal or better results.

This report was submitted in fulfillment of Contract No. 68-03-3038 by Radian Corporation under the sponsorship of the U.S. Environmental Protection Agency. This report covers the period of February 1982 through August 1984.

CONTENTS


Foreword . . . . . iii
Abstract . . . . . iv
Figures . . . . . vi
Tables . . . . . vii

1. INTRODUCTION . . . . . 1
   1.1 Background . . . . . 1
   1.2 Technical Objective . . . . . 2
   1.3 Program Approach . . . . . 2

2. SUMMARY OF RESULTS, CONCLUSIONS, AND RECOMMENDATIONS . . . . . 3
   2.1 Results and Conclusions of the Feasibility Evaluation . . . 3
   2.2 Results and Conclusions of the Laboratory Testing . . . . . 4
   2.3 Results and Conclusions of Field Testing . . . . . 7
   2.4 Recommendations . . . . . 9

3. REVIEW AND SELECTION OF ALTERNATE MEASUREMENT CONCEPTS . . . . . 11
   3.1 Review of Material Balances . . . . . 12
   3.2 Review of Tracer Concepts . . . . . 20
   3.3 Review of Modeling Concepts . . . . . 25
   3.4 Review of Approximation or Assumption Concepts . . . . . 26

4. LABORATORY TESTING . . . . . 29
   4.1 Experimental Approach . . . . . 29
   4.2 Experimental Work . . . . . 33
   4.3 Experimental Results and Discussion . . . . . 43
   4.4 Quality Assurance and Quality Control . . . . . 55

5. FIELD TESTING . . . . . 57
   5.1 Test Site Description . . . . . 57
   5.2 Testing Approach . . . . . 62
   5.3 Test Methods and Procedures . . . . . 67
   5.4 Results and Discussion . . . . . 71
   5.5 Quality Assurance and Quality Control . . . . . 89

REFERENCES . . . . . 95

APPENDICES . . . . . 97

FIGURES


| Number | | Page |
|---|---|---|
| 1 | Typical Coating Operation Stream Flow and Emissions | 13 |
| 2 | Test Apparatus for Capture Efficiency Laboratory Study | 35 |
| 3 | Detailed Plant-Wide Flow Diagram | 59 |
| 4 | Coating Area Flow Diagram | 63 |
| 5 | Simplified Plant-Wide VOC Flow Diagram | 65 |
| 6 | Range of Error for Means of Multiple Measurements of Coating Line Liquid/Gas Closure | 90 |
| 7 | Response Factor Variations with Compositions for a Byron 401 | 93 |

TABLES


| Number | | Page |
|---|---|---|
| 1 | LIQUID GAS-PHASE TESTING RESULTS | 15 |
| 2 | SUMMARY OF VOC CAPTURE EFFICIENCY SAMPLING/ANALYTICAL METHODS | 37 |
| 3 | TEST MATRIX FOR FLOW RATE INTERACTION EFFECTS | 38 |
| 4 | TEST MATRIX FOR MASS BALANCE EXPERIMENTS | 40 |
| 5 | TEST MATRIX AND RESULTS FOR FLOW RATE INTERACTION EFFECTS | 44 |
| 6 | ANALYSIS OF GAS PHASE FLOW RATE TEST RESULTS | 46 |
| 7 | LIQUID/GAS MASS BALANCE CLOSURES | 48 |
| 8 | ANALYSIS OF MASS BALANCE TEST RESULTS | 49 |
| 9 | VOLATILE CONTENT OF COATING MIXTURES | 53 |
| 10 | COMPARISON OF RF FACTORS ON CLOSURES FOR MEK/TOLUENE MIXTURE EXPERIMENTS | 54 |
| 11 | SUMMARY OF SAMPLING/ANALYTICAL METHODS | 68 |
| 12 | LIQUID AND GAS MASS FLOW RATES AND CAPTURE EFFICIENCIES FOR THE COATING ROOM | 72 |
| 13 | CAPTURE EFFICIENCY AVERAGES BY DAY | 76 |
| 14 | CAPTURE EFFICIENCY AVERAGES BY SLURRY BATCH | 77 |
| 15 | GAS-PHASE MASS FLOW RATES AND MATERIAL BALANCES FOR THE SLA SYSTEM | 79 |
| 16 | SLA GAS-PHASE MATERIAL BALANCES USING DAILY AVERAGING PERIODS | 82 |
| 17 | SLA GAS-PHASE MATERIAL BALANCES USING SLURRY BATCH PERIODS | 83 |
| 18 | LIQUID MASS INVENTORY DATA | 85 |
| 19 | INPUT VALUES FOR MONTE CARLO SIMULATION OF COATING LINE LIQUID/GAS CLOSURE MEASUREMENTS | 88 |
| 20 | BYRON 401 RESPONSE FACTOR VARIATIONS WITH COMPOSITION | 92 |

# SECTION 1

# INTRODUCTION

The U.S. Environmental Protection Agency initiated the work described in this document to explore alternate methods for determining volatile organic compound (VOC) capture efficiency in industrial surface coating facilities. The information obtained from this program will be used to provide additional technical support for EPA regulatory activity in the area of VOC emissions from surface coating operations. The data obtained will also augment the existing VOC control technology data base.

The remainder of Section 1 provides information pertaining to the program background, objectives, and study approach. Section 2 presents a summary of the results, conclusions, and recommendations arising from the study. Section 3 reviews the potential alternate capture efficiency measurement techniques considered. Sections 4 and 5 present the experimental testing of the liquid/gas-phase material balance method in the laboratory and under field conditions.

## 1.1 BACKGROUND

In recent years, the U.S. Environmental Protection Agency (EPA) through the Office of Air Quality Planning and Standards (OAQPS) has developed gaseous emission standards for new surface coating operations. The new source performance standards (NSPS) regulate emissions of VOCs from these operations. The term "surface coating industry" is meant to include any operation which applies by spraying or roll coating or some similar method a coating which is dissolved or suspended in a solvent. The solvent may be organic or aqueous or a combination of both.

Most of the surface coating NSPSs are written as emission limits based on the coating solids applied. Compliance with these standards may be met by using low solvent coatings within the limits of the standard. Compliance may also be met by installation of add-on controls and demonstration of the overall VOC reduction required to meet the emission limits. Some of the regulations, specifically those for roll coating operations, offer an alternative using add-on controls and demonstration of overall VOC reduction efficiency (ORE) in excess of a minimal established value. Operations utilizing add-on controls must conduct an initial performance test demonstrating the system's ability to reduce the emissions by either the calculated or minimum value. Compliance is later continually determined by monitoring certain normal operating parameters of the process and control system, which are indicative of the control performance.

Performance demonstration testing is normally conducted using material balance methods around the regulated process and control system. In many surface coating plants, carbon adsorption or recovery type control devices are utilized because of the economic advantages. In these cases, performance demonstration testing usually involves a liquid-phase material balance around

the coating line and control device, i.e., comparison of liquid VOC used with that recovered, over a 30-day period.

Other plants utilize destruction type control devices and cannot conduct a liquid-phase material balance for demonstration of performance. Any test method for demonstrating ORE, other than a liquid-phase material balance, requires a knowledge of the fraction of emissions actually captured by the capture system, as well as the fractional destruction of the captured emissions by the control device. The fractional capture is called "capture efficiency" and the fractional destruction is called "control device efficiency". The product of the two yields the overall reduction efficiency.

Capture efficiency has been attempted by several methods in the development of the NSPSs. The only method that has produced satisfactory results is the gas-phase material balance method, utilizing an enclosure around the regulated coating line to contain and direct fugitive emissions to a single measurable stream. Where the regulated coating line is not isolated within a permanent enclosure, the EPA has indicated in some standards, such as that for the pressure sensitive tape and label industry, that a temporary enclosure should be erected and used to collect fugitive emissions for measurement. This method may be costly and inconvenient. Therefore, this study has been initiated to explore possible alternate methods for determining capture efficiency, which might be less costly and more convenient.

## 1.2 TECHNICAL OBJECTIVE

The objective of this study was to develop an alternate technique for measuring VOC capture efficiency. The capture efficiency, as determined by this technique, and the control device efficiency, as determined by previously developed techniques, may then be combined to determine the overall effectiveness of a control system on emissions from a surface coating operation.

## 1.3 PROGRAM APPROACH

The study was designed and conducted in two phases. Phase I was primarily a review of existing information/recent studies, and development and evaluation of the feasibility of alternate assessment methods. Phase II was the detailed testing phase of the project and involved testing the most feasible method, as determined from Phase I.

## SECTION 2

## SUMMARY OF RESULTS, CONCLUSIONS, AND RECOMMENDATIONS

In the study of alternatives for determining process capture efficiency, alternate concepts were reviewed and evaluated for feasibility, and the most acceptable alternative was tested. There were three major segments of the study:

- Review and evaluation of alternatives,
- Laboratory testing, and
- Field testing.

### 2.1 RESULTS AND CONCLUSIONS OF THE FEASIBILITY EVALUATION

Alternate measurement concepts reviewed and considered included:

- Material balance methods,
- Tracer concepts,
- Modeling, and
- Other approximation techniques.

#### 2.1.1 Results of the Feasibility Evaluation

A review of available information sources regarding alternate measurement methods found surprisingly little supportive information in any area other than material balances and tracers. Of the alternatives reviewed, several were considered feasible, but the liquid/gas-phase material balance and the tracer gas concepts were the most acceptable approaches.

A review of past tests involving liquid and gas-phase measurements was inconclusive regarding the applicability of liquid/gas material balances to field determinations of capture efficiency. However, the majority of the tests were not specifically designed around a liquid/gas material balance, involved short non-steady state test periods, or had other shortcomings in the measurement of the mass flow variables. Several tests involving longer test periods and semi-steady state operating conditions did yield results which appeared to be representative of the capture efficiency. Therefore, the potential applicability of this method seems limited to either steady-state or relatively long term test conditions. Like the gas-phase methodology, the liquid/gas-phase material balance approach also can only be applied to operations which do not use zone incineration or direct firing of the drying oven.

Inert tracer gases, such as sulfur hexafluoride ($SF_6$), have been used extensively in other air movement and monitoring studies. Some preliminary studies indicate that the tracer gases might be used successfully to determine hood capture efficiency and, in turn, the process capture efficiency. The determination of hood capture efficiency appears very straightforward using

tracer gases. However, determination of process capture efficiency also requires knowledge of the mass of emissions generated from the various process segments, which is generally not available. A potential advantage of the tracer gas method is the potential application to all operations, including those employing zone incinerated or direct fired drying ovens.

### 2.1.2 Conclusions of the Feasibility Evaluation

A comparison of the material balance and the tracer gas concepts concluded that both methods might be feasible and potentially applicable, but that the material balance approach is generally more acceptable. This conclusion was based on the premise that direct measurements are more readily accepted than indirect determinations, and that the material balance methods are further developed than the tracer methods. Therefore, a decision was made to conduct further evaluations and developmental testing of the liquid/gas-phase material balance methodology.

The experimental testing of the liquid/gas-phase material balance method was divided into two phases: (1) laboratory testing and (2) field testing. The laboratory testing was necessary because of the difficulties encountered in assessing the test methodologies and results from previous field tests. It was considered strategically important to begin testing under the simplest conditions and work up in complexity, and to be able to control and measure all streams for verification of test results. The laboratory approach met both of these criteria.

## 2.2 RESULTS AND CONCLUSIONS OF LABORATORY TESTING

The liquid/gas-phase material balance method of determining process VOC capture efficiency was evaluated through a series of laboratory experiments. The variability to be anticipated from the test methodology was investigated in order to assess the actual feasibility and expected test performance under the most ideal field conditions.

Individual methods were also evaluated in the two major sets of experiments conducted, as shown below:

Gas Flow Rate Experiments

- EPA Method 2 for the determination of gas flow rates,

Mass Balance (Evaporation) Experiments

- EPA Method 25A for VOC determinations by total hydrocarbon analysis,
- EPA Draft Method 18 for VOC determinations by GC/FID,
- NIOSH Method 127 VOC determinations by charcoal tube adsorption, and
- EPA Method 24 for determination of volatile content of coating mixtures.

### 2.2.1 Gas Flow Rate Experiment Results

The gas flow rate experiments were conducted according to a fractional factorial test matrix. The objective of the study was to evaluate the main and low order interaction effects associated with variables involving EPA Method 2 type flow rate determinations. The variables tested included pitot tube type, the pressure measuring device, the sampling location, the relative flow rate, and the personnel conducting the test.

Analysis of the gas flow rate data indicated excellent precision for all measurements with coefficients of variation not exceeding 4%. The greatest variability in the data was seen at the lowest flow rate, where minor discrepancies have a more pronounced effect.

Analysis of variance (ANOVA) techniques were used to test the statistical significance of first and second order effects from each of the variables (e.g. instrumentation used, location of measurement, operator). In only a few cases were any of the interaction effects considered statistically significant. The analysis indicated differences of marginal significance ($\alpha = .10$) in the data obtained from different type pitot tubes at the lowest flow rate and from differences in pressure measuring devices at the middle flow rate ($\alpha = .05$). The combination of S-type pitot tube and Magnehelic® Gauge produced significantly different data ($\alpha = .01$) from other combinations at the highest flow rate.

Overall, no single variable or combination of variables appears to have any practical significance. However, it is considered advisable to avoid combining the S-type pitot and Magnehelic®, particularly at higher flow rates.

### 2.2.2 Mass Balance (Evaporation) Experiment Results

The mass balance experiments provided an opportunity to assess the ability to close liquid/gas material balances using the available methodology, while conducting comparative testing of three different VOC analysis methods and testing of a method for the volatile content of the coating. Varied solvent amounts, solvent types, and gas flow rates were introduced into the testing to simulate some important field variables.

The test system was designed as a simple flow-through evaporation chamber, thus providing 100% capture and minimizing the number of measurement parameters. Therefore, a known-capture efficiency was established for comparison with the measured and calculated values, and sources of error in measurement were reduced to the lowest level.

Method 25A closures were by far the most successful in this set of experiments. Accuracy, bias, and precision were evaluated for the pure solvent and the commercial mixture experiments as separate groups. Accuracy seems more than adequate for each group since the mean closure values were, respectively, 99.9% (88.5-110%) and 102.2% (93.5-119). Bias for either group was not statistically significant, since 100% was included within the 95% confidence interval in both cases. Precision, or variability, estimates for the two groups were excellent, since the coefficients of variation were 5.9 and 8.9%,

respectively. Test results for the commercial coatings test runs were less accurate than pure solvent runs, probably due to the smaller change in liquid mass and lower SLA concentrations.

The solvent amount was the only variable found to have any statistically significant impact on the Method 25A data. As a practical matter, this marginally significant effect would be difficult to explain since the mid-level (1.0 liter) results seem to deviate from the low and high level results. Thus, none of the variables nor combination of variables seems to have any great effect on the closure technique results.

Method 18 closure data were evaluated for accuracy, bias, and precision in the same manner as the Method 25A data. Based on mean closure values of 93.6% (73-264%) and 106.8% (86.2-186%) for the pure solvents and commercial mixture tests, respectively, the method appeared to be only marginally accurate. The wide 95% confidence intervals (83.1 to 104.2% and 71.1 to 142.6%) tended to discount bias as the primary problem. There was not sufficient evidence in the Method 18 closure results to indicate significant main or interaction effects, at least to the $\alpha = 0.10$ level. However, the variability estimates as measured by the coefficient of variation indicated that the particular methodology or instrumentation used was not adequate for measuring VOC capture efficiency during the laboratory testing phase.

Two possible explanations were postulated regarding the wide ranging Method 18 data First, detailed review of the THC concentrations for each run showed variations with substantial up and down swings. The 7-minute interval data obtained by the Method 18 analyzer very likely missed a number of the peaks and/or valleys. Second, during some of the runs, it was apparent that the sensitivity of the Method 18 analyzer changed during the run. At one point, the analyzer's detector jet was mechanically cleaned and the sensitivity rose dramatically. The extent of this problem was not quantified.

Full statistical analysis was not performed on the charcoal tube data. However, the data indicate that the method is not adequate for performance testing. The most serious problem associated with this method seems to be its variability. As measured by the coefficient of variation, this was 62.2%. The variability could not be explained based on the available data.

### 2.2.3 Conclusions of Laboratory Experiments

The laboratory testing of the liquid/gas-phase material balance methods concluded that reasonable closure results and capture efficiency determinations can be obtained under controlled flow conditions. Gas flow rates determined by EPA Method 2 are not significantly impacted by the instruments used nor the operator, and they are suitable for use in liquid/gas material balance type capture efficiency determinations. EPA Method 25A was found to be the most suitable method for measuring gaseous VOC concentrations of the three examined. Based on these findings, it was recommended that the methods be further evaluated in a rather non-complex field environment.

## 2.3 RESULTS AND CONCLUSIONS OF FIELD TESTING

VOC process capture efficiency determinations were made at an industrial surface coating plant manufacturing magnetic tape and using a two-component solvent system. Mass balance closure techniques and liquid/gas conversion methodologies were employed. Major efforts were focused on:

- Coating Area Capture Efficiency Measurement,
- Error Analysis in Capture Efficiency Determinations, and
- Other Material Balances.

### 2.3.1 Results of Coating Area Capture Efficiency Measurements

Measurement of VOC mass flow rates were made for the liquid (slurry) applied and the captured gas from the coating area of the plant. Liquid measurements included slurry feed tank volume, slurry density, and slurry volatile fraction. Gas phase measurements of the capture stream included flow rate, VOC concentration, temperature, and pressure.

Over a test period of 114 hours, consisting of 6 discrete batches, hourly determinations of VOC capture efficiencies varied significantly using both EPA Method 25A and Draft Method 18 data for total gaseous hydrocarbon (THC). However, when averaging the data over approximately 24 hour periods, variability decreased. Over the entire test period, the mean capture efficiency was 106.7% with a coefficient of variation (CV) of 7.4%, using Method 25A data. Using Method 18 data, the mean capture efficiency was 105.1% with a CV of 1.3%. Evaluating the data on a batch basis led to a mean capture efficiency of 103.0% and a CV of 4.6%, using Method 25A data. In each case the calculated mean capture efficiency was higher than expected.

In order to estimate the reliability of the capture efficiency results obtained, a complete error analysis was performed. Estimates for measurement errors were provided by an external audit or determined from repetitive measurements.

Average values and estimated errors were input to a Monte Carlo simulation to obtain a series of 400 coating room closures that were statistically related to the plant data set. This exercise indicated a relative bias of -3.9% in the coating room closure data. Furthermore, the analysis showed that a single measurement has a 38% probability of being within $\pm$5% of its true value. Finally, if 3 individual sets of closure measurements are made, the average value should be within $\pm$10.7% of the true value with a 95% confidence limit. For six measurements, the average value would be within $\pm$7.6%. Using the data collected at this site, it appears that the limits can only be narrowed to approximately $\pm$4% of the true value.

An obvious discrepancy existed between the high results obtained in the field test and the negative bias indicated by the error analysis. However, the indicated bias in the error analysis comes strictly from an audit of the total hydrocarbon analyzers and does not include any opposing bias that might be

associated with the other measurements. Based on a review of the process streams measured, the measurement methods, and quality assurance program, there is no reason to believe that any source of VOC went unmeasured or that any measurement bias existed that would cause the higher measurement values. Therefore, the discrepancy is unexplainable.

### 2.3.2 Results of Other Material Balance Determinations

Liquid inventory data were obtained for all storage and process areas. The density and volatile fraction of each liquid were also determined.

Gas-phase determinations were made of VOC content, flow rate, temperature and pressure for the storage tank vent collection stream, the main solvent laden air (SLA) stream, and the carbon bed stack exhaust in addition to the same measurements for the capture stream as described in the previous section. VOC measurements were made by EPA Methods 18 and 25A.

The data were evaluated through various combinations to determine the acceptable methods of viewing capture efficiency and/or mass balance closures. One of the most exhaustive investigations involved a comparison of the main SLA stream mass flow rate with the sum of the capture and vent stream mass flow rates. These two comparative masses were expected to be equal, since the vent and capture stream combine to form the main SLA stream. Results of this comparison yielded 94.3% closure with a coefficient of variation of 4.3% for Method 25A data and 24-hour averaging. For the Method 18 data, average closure was 99.4% with a 9.1% coefficient of variation.

Further evaluation of this data on a slurry batch basis produced closure results of 92.9% with a coefficient of variation of 2.5%, using Method 25A data. Method 18 data provided an average closure of 96.3% and a coefficient of variation of 8.8%. The evaluation on a batch basis did not provide noticeable improvement. This is probably related to the continuous steady state nature of the vent stream.

A potential source of error in the determination of the mass flow rates and mass balance closures above may be associated with the Method 25A analyses based on an erroneous assumption that all streams contained a 75/25 ratio of the two solvents. The composition of the vent stream is known to have varied from this ratio to a higher ratio, causing measured values to be biased low. This potential source of error possibly explains part of the discrepancy in the Method 25A mass balances, but it does not appear significant enough to account for the total differential.

A plant-wide liquid inventory was conducted over the test period based on measurements at approximately 8-hour intervals. Added to the measured liquid mass were the only known fugitive sources, the carbon adsorber stack outlet, the solvent recovery water discharge, and the floor sweep exhausts within the plant. The purpose was to develop a total accountable VOC inventory. Running a mass balance closure indicated that 95% of the VOC had been accounted for. Other than product retention, an adequate explanation for the discrepancies could not be found.

Several other comparisons of data were made. Many of these involved the amounts of liquids transferred through metered pipes. In most cases, the multiple combination comparisons indicated fairly wide error margins, in the 20% range.

### 2.3.3 Conclusions of Field Testing

It was concluded from the field test that estimates of the VOC capture efficiency around a non-complex system can be obtained within approximately ±10% of the true value, based on an error analysis conducted on the field test in this study. The accuracy of the determinations can be improved only to a limited degree by increasing the number of tests. It is expected that variability of data will increase with the complexity and non-steady state conditions at most plants causing even wider confidence intervals.

The confidence interval is expected to be much narrower for the same site using calculations based on the EPA proposed gas-phase material balance and an exhausted measurement enclosure. This is primarily due to the form of the gas-phase material balance equation. In the equation, the numerator and denominator are both composed primarily of the same measurement value, therefore, minimizing the impact of measurement bias or variability on the results.

## 2.4 RECOMMENDATIONS

Presently, there is no apparent alternate method for measuring VOC capture efficiency which would produce data equal or better in quality to that of the gas-phase enclosure method. However, the gas-phase methodology, like the liquid/gas methodology, is not applicable to operations employing direct fired ovens or zone incinerated ovens. In these cases an alternate approach must be used unless permanent total enclosures are required.

In this regard, criteria must be developed on which to base the acceptability of an alternate method. This criteria should establish the required accuracy of measurements and confidence limits for calculated capture efficiency values.

From this study, it appears that a tracer gas method would be the most acceptable alternative. However, this methodology is not fully developed or tested. Steps in the process of developing such a method should include the following:

- Identify or establish mass emission factors or rates for typical surface coating VOC sources.
- Conduct a laboratory comparison between the tracer gas mass balance approach and the tracer gas relative measurement approach.

- Conduct a laboratory evaluation to determine the most acceptable tracer gas release technique (e.g. manifold, single point release, or multiple individual releases at different points on a source surface).

- Determine the number of tests, release points, release rates, and measurements required to obtain the desired accuracy.

- Conduct a test involving direct flame contact with the $SF_6$ to evaluate the impact of direct fired ovens on test results.

## SECTION 3

## REVIEW AND SELECTION OF ALTERNATE MEASUREMENT CONCEPTS

In the process of reviewing and selecting alternatives, four discrete tasks were conducted:

- Identification and review of pertinent literature and other information.
- Review of past EPA sponsored material balance tests and test methods.
- Formulation of conceptual techniques for determination of capture efficiency.
- Evaluation of the feasibility of alternate techniques for the determination of capture efficiency.

These tasks involved the search and review of literature in 9 computer bases and off-the-shelf literature, numerous telephone contacts with knowledgeable authorities, review of 31 field tests conducted on surface coating facilities, and field visits and reviews at 10 industrial surface coating sites. Information obtained during these review and evaluation steps and the contractor's in-house technical knowledge led to the formulation and the feasibility evaluation of the conceptual techniques.

The computer bases searched included the following:

- Engineering Index
- Surface Coating Abstracts
- NTIS
- APTIC
- NIOSHTIC
- Pollution Abstracts
- Conference Papers Index
- SSIE (Research in Progress)

Sources of information which were selected and reviewed from these bases and from the shelf are presented in Appendix A.

The review of previously conducted field tests are summarized later in this section. Individual reviews of all tests are presented in Appendix B.

The methods conceptualized and reviewed included both direct and indirect methods. Direct methods are material balance techniques, where the masses of VOC in specific streams are measured and compared in order to calculate capture efficiency. Indirect methods utilize techniques where the VOC masses are not measured (e.g. tracers, modeling, or other approximation techniques).

The following sections present brief descriptions of the potential alternate methods, evaluations of the methods, and conclusions regarding the feasibility and applicability of each method to surface coating operations.

## 3.1 REVIEW OF MATERIAL BALANCES

Possible material balance methods applicable to capture efficiency determination are gas-phase material balances and liquid/gas-phase material balances. All previous EPA sponsored work and tests involving capture efficiency determinations have utilized material balance techniques.

Figure 1 shows a typical surface coating operation and the VOC mass flows in and around the coating line and control device. This figure and the denoted VOC streams will be referred to throughout the following discussions.

### 3.1.1 Gas-Phase Material Balance

The gas-phase material balance method using a permanent or temporary enclosure for measuring emissions is presently the only method recommended by EPA for demonstrating capture efficiency. From past efforts and evaluations, it is obvious that a gas-phase balance can only be conducted using an exhausted enclosure, as described by the EPA. Therefore, no alternate gas-phase testing methodology is proposed. Referring to Figure 1, capture efficiency by the gas-phase method is calculated as shown in Equation 1 below:

$$\text{Capture Efficiency (\%)} = \frac{C}{C + C'} \times 100 \qquad (1)$$

### 3.1.2 Liquid/Gas-Phase Material Balances

In the liquid/gas-phase material balance approach, the mass of liquid VOC applied at the coater is used to represent the mass of total emissions. Therefore, the methodology involves a comparison of liquid VOC used at the coaters and the gaseous VOC emission captured and directed to the control device. Referring to Figure 1, capture efficiency by the liquid/gas material balance method would be calculated as shown in Equation 2 below:

$$\text{Capture Efficiency (\%)} = \frac{C}{B} \times 100 \qquad (2)$$

The liquid VOC (solvent) mass used at the coater can be determined by monitoring the mass or volume of coatings used during the test and by determining the VOC content of the coating material. The VOC mass flow in the capture stream can be determined by measuring the gas flow in the stream and the VOC content of the gas.

This particular approach to determine capture efficiency is rather simple in concept since it requires the measurement of only two streams, liquid solvent in and gas captured. It also requires none of the time or expense

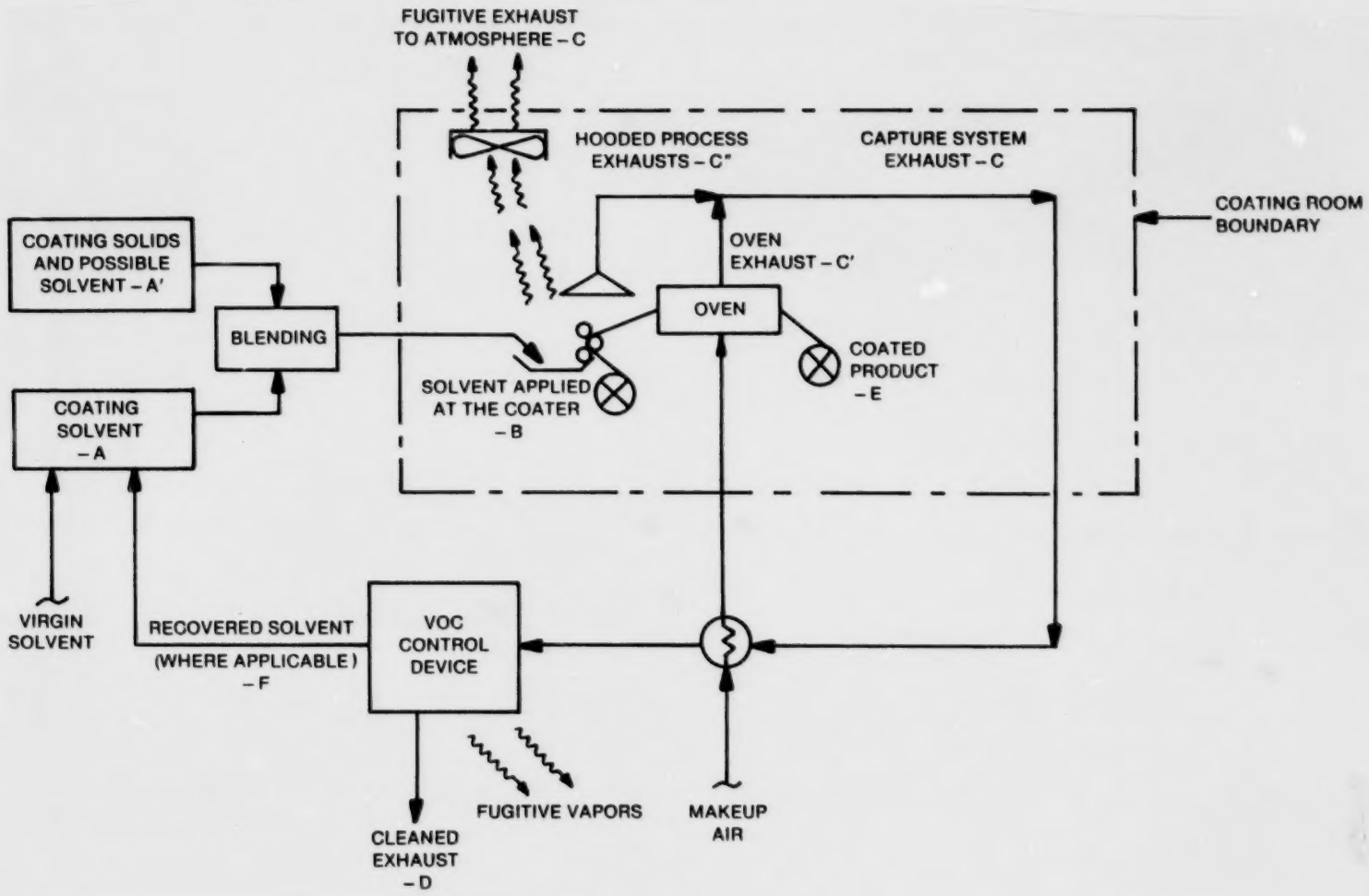


Figure 1. Typical coating operation stream flow and emissions.

involved with erecting an enclosure, nor does it involve the concerns that may arise with regard to creating an altered test environment potentially associated with a temporary enclosure test.

3.1.2.1 Evaluation of Methodology--

Theoretically, the product of the liquid/gas-phase capture efficiency and the control device efficiency is equivalent to the liquid-phase material balance equation for determination of overall reduction efficiency. Both concepts similarly ignore any VOC retained in the product and assume it to be part of the emitted VOC.

From an error analysis viewpoint, the capture efficiency determinations using the liquid/gas-phase equation are highly susceptible to variability. Both variables in the equation will most likely be large in magnitude, and the calculations using this equation will be nearly equal in sensitivity to both. Since the values of the variables will be determined by different measurement methods on different streams, the impact of measurement inaccuracies may compound in the final results. Therefore, it can be concluded that accurate determination of capture efficiency by the liquid/gas-phase approach depends critically on the precision and accuracy of the individual measurements.

In evaluating the test methodology, thirteen tests involving liquid/gas-phase measurements were reviewed, ten of which had adequate data to attempt a capture efficiency determination. Table 1 presents a summary of the material balance closure results obtained from these tests. Reviews of the individual tests are presented in Appendix B. In most tests reviewed, the capture efficiency results did not compare well to expected efficiencies or efficiencies determined by other proven methods (e.g. long term liquid-phase testing of overall efficiencies). However, several tests did appear to provide accurate representations of the expected efficiencies.

In many cases, there was not substantial detail to determine the reasons for the test failures. However, from the information in some of the tests the following were derived as potential causes of variance:

- inadequate characterization of solvent and coating composition,
- difficulty in obtaining accurate measurements of liquid coating material used at the line tested,
- use of intermittent gas stream test methods and monitoring at streams with non-ideal locations, and
- short term tests involving non-steady state conditions.

Each of these is discussed to some degree in the following paragraphs.

Characterization of coating solvent content--Since the solvent content of the liquid coating represents one portion of the determination of the VOC mass used (total VOC emissions), the accuracy of this value is critical. Many of the plants tested used manufacturers data and plant formulation records for determining the solvent (VOC) content of the coating rather than conducting separate analyses. Past experience has shown that manufacturers' data are not

TABLE 1. LIQUID GAS-PHASE TESTING RESULTS

| Plant | Industry | VOC Type(s) | Control Method | Capture Efficiency (%) | Control Efficiency (%) | Overall[a] Efficiency (%) | Time Averaging Period | Method of Analysis | Reference |
|---|---|---|---|---|---|---|---|---|---|
| 7 | Publication rotogravure | Toluene | Carbon adsorption | 74.2[c] | 124.5[c] | 92.4[c] | NA | Analysis of gas streams with semi-continuous FID and grab sample GC; analysis of liquid streams for solvent content. | 1 |
| 8 | Publication rotogravure | Toluene, xylene | Carbon adsorption | 58.7[c] | 144.3[c] | 84.7[c] | NA | Analysis of gas streams with semi-continuous FID, GC/FID, and Method 25; analysis of liquid streams for solvent content. | 2 |
| 11 | Paper | Toluene, ethyl acetate, isopropanol | Carbon adsorption | 94 | 98 | 92 | 6 hours | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 3 |
| 20 | Vinyl | NA | Carbon adsorption | 60.5[b] | NM | NM | 50 hours | Continuous FID analysis of gas streams, usage rate and solvent content of ink. | 4 |
| 23 | PSTL | NA | Thermal incineration carbon adsorption | 40/159[c,d] | NA | NA | NA | Bag samples with FID, semi-continuous FID, and EPA Method 25 for gas-phase analysis | 5 |
| 24 | Metal coil | NA | Thermal incineration | NM | NM | 99.9[c] | NA | GC/FID of incinerator effluent; solvent usage rate. | 6 |
| 25 | Metal coil | Aromatic hydrocarbons, glycol ethers | Thermal incineration | NA | NA | NA | NA | Analysis of gas streams with continuous FID and EPA Method 25 | 7 |
| 26 | Paper | NA | Thermal incineration | 94-98 | 94-96 | 91-93 | 3 hours | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 3 |

TABLE 1. LIQUID GAS-PHASE TESTING RESULTS
(continued)

| Plant | Industry | VOC Type(s) | Control Method | Capture Efficiency (%) | Control Efficiency (%) | Overall[a] Efficiency (%) | Time Averaging Period | Method of Analysis | Reference |
|---|---|---|---|---|---|---|---|---|---|
| 27 | Paper | Toluene, others | Carbon adsorption | NM | 79 | NM | 6 hours | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 3 |
| 28 | Metal can | Cello-solve acetate, butyl cel-losolve, xylene, isophorone, others | Thermal incineration | 221[c] | 73 | NA | NA | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 3 |
| 29 | Metal can | Xylene, diacetone alcohol, MIBK, iso-phorone, butyl cel-losolve | Thermal incineration | 174[c] | 26 | NA | | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 3 |
| | | | Catalytic incineration | 90 | 49 | 44 | | | 8 |
| 30 | Beverage can | Cello-solve acetate, others | None | 87.8 | NM | NM | 195 mins. | Analysis of gas streams with Method 25; analyis of liquid streams for solvent content. | 9 |
| 31 | Beverage can | NA | Thermal incineration | 79 | NM | NM | 137 mins. | Analysis of gas streams with Method 25; analysis of liquid streams for solvent content. | 9 |

[a] Overall Efficiency = Capture Efficiency X Control Efficiency
[b] data are reported to be inconclusive
[c] questionable data
[d] FID analysis of gas stream
NA = data not available
NM = not measured
PSTL = pressure sensitive tapes and labels
FID = flame ionization detection
GC = gas chromatography
MIBK = methyl isobutyl ketone

always accurate and are often generalized. On the otherhand, plant formulation records provide accurate coating data if the materials are measured with reasonable precision. In either case, the solvent content at the time of mixing does not necessarily accurately represent the solvent content evaporated in the coating room, particularly if the coating is held for any period of time before transfer.

Another typical source of error related to solvent content may be involved when the coating is recirculated between the coating reservoir and the coating pan. Use of manufacturer or plant formulation data combined with the amount of coating used will not reflect the VOC lost from any coating not applied but continuously recirculated, the significance of this undetermined volume is unknown.

Addition of solvent to the coating reservoir for viscosity control is common and may be frequent at some plants. These added amounts also must be considered in the solvent content of the coating. Because of these adjustments and the other potential sources of error above, it seems critical in most short term tests to monitor the solvent content of the coating frequently.

Mass of liquid coating used--The amount of liquid coating lost or used represents the other half of the critical liquid VOC measurements. A number of options exist for measuring the liquid use including: determination of the applied coating weight or thickness and the web speed, depth gauging of coating vessels and subsequent volume determinations, and metering of the coating components to the coating line. All of the coating flow measurement techniques are made difficult by the complex flow arrangements (e.g. recirculation and multiple vessels in the flow loop).

Depth gauging of coating vessels is by far the most popular and most applicable method in the tests reviewed and plants visited. Depth gauging can be applied to process configurations employing direct delivery of coatings to the application point or those utilizing batch vessels, coating pans, and recirculation at the coating line. The precision and accuracy of the volume determinations by depth gauging are uncertain and are definitely affected by the symmetry of the vessel, the depth to width ratio of the vessel, and the presence of objects occupying volume within the vessel (e.g. agitators, pumps, and hoses). No specific studies have been conducted to determine the effects of these items, nor do test reports contain sufficient detail regarding these measurements to make an evaluation of their impact on the test measurements. In most plants visited, it was agreed that objects occupying space within the depth measurement zone are fairly insignificant (e.g. agitator blades) or are removable during the measurement period.

The applied coating thickness or weight may be determined in several different ways. Most of the coating thickness gauges produce relatively imprecise data, with the possible exception of the continuous beta gauges. Applied coating weight determinations reportedly have been successful where the coating weight is significant with respect to the weight of the substrate, and the coating weight is determined by the difference in the weight of a web roll before and after coating. Using the applied coating weight or thickness and

the associated solvent content of the coating is only representative of the total VOC emissions if the coating material is delivered directly to the application point without recirculation. Otherwise, the amount of applied coating will not represent the evaporated solvent lost from the coating vessel or from recirculation at the process line. Visits at a variety of surface coating plants indicate direct feed of the liquid coating without recirculation is not typical.

Metering of coating material to the coating line for determining the volume of coating material subjected to vaporization may have limited application in some industries. One magnetic tape plant indicated that the application of meters may be limited. The company claims that they are not suited for handling highly viscous materials or abrasive components (e.g. iron oxide in magnetic tape coating). A metal coil coating plant representative had concern that the accuracy of measurements would be affected by changes in the material density. However, in this study some publication rotogravure plants were found to use metering of coating components to the line, since they use large quantities of the same components. Metering, in these cases, is limited to individual component lines feeding intermediate mixing or holding reservoirs at the line. Reasonable accuracies have been experienced in metering the components to the vessels, but depth gauging or another technique are ultimately used to determine the volume or mass actually transmitted from the vessel to the coater during the test period unless start and stop of the test are scheduled at identical reference points (e.g. when the intermediate reservoir is filled).

An untested option for measuring flow of liquid coating material to the coating line and obtaining initial and final measurements is a mass determination approach. Rather than measure the volume of the coating vessel at the start and finish of the test, the vessel could be weighed using the same basic flow theory as that in the volumetric approach. Mass measurements at the start and finish of the test could be made if the vessel is placed on a scale or balance or mounted on load cells. Advantages of the mass measurement method over the volume determinations are that the measurements are not affected by the dimensions or symmetry of the vessels or by items occupying space in the vessel.

Gas-phase flow rates and concentrations--The mass of gaseous VOC captured is determined by the product of the gas flow rate measurements and the measurements of the VOC content of the gas stream. In most tests reviewed, the VOC concentration was determined by collection of full term integrated samples (EPA Method 25) or by semi-continuous monitoring (EPA Method 25A), and the gas flow rate was typically determined by one or two pitot traverses during the test period.

In most capture systems the flow rate remains fixed while the concentration fluctuates due to process fluctuations. As long as the operating conditions are nearly steady state, semi-continuous monitoring and continuous sampling will account for any minor concentration peaks or valleys that may occur. However, where non-steady state conditions exist, semi-continuous monitors may not pick up rapid peaks and valleys and a variance may result in the mass flow determinations.

In other capture systems, monitors and automatic controls hold the concentration of the gas stream steady by varying the gas flow rate. Since the gas flow is typically not measured continuously, significant fluctuations could take place unnoticed creating a major variance in mass flow determinations, but they may be significant. Where testing involves capture streams with potentially fluctuating flow rates, continuous monitoring of the flow rates (velocity) will provide the proper adjustment factors for mass flow determinations.

From the tests reviewed, it was noted that some did not follow EPA reference methods outlining selection of gas flow measurement points in nonturbulent zones. The accuracy of pitot measurements may be severely affected by turbulent conditions. There was not sufficient information in each test to assess the presence and effect of this potential source of variance, but test results involving poor measurement locations may have been significantly impacted. From plants visited during this study and past experience, it is realized that it is not unusual to encounter poor measurement locations in existing systems. However, NSPS performance demonstration testing will be conducted on systems which will have measurement locations meeting EPA optimal criteria, as required by NSPSs, and in those tests it should not present a significant source of error.

Length of test--Most of the tests reviewed were conducted over relatively short test periods involving non-steady state conditions. When the sample periods were relatively short (e.g. 3 hours), the tests with the greatest success were those which were conducted during steady state operations. One test conducted over a relatively short period under steady state operations produced acceptable test results (3).

Another test involving test periods of different lengths and non-steady state conditions produced results indicating that closure data become less variable when accumulated and averaged over longer test periods (4). In this test, it appears that the variability in closure results reached a relatively insignificant level at approximately nine hours. It is expected that the required averaging period will differ for operations involving different operational parameters.

3.1.2.2 Assessment of Feasibility--

It was concluded from the review that the liquid/gas-phase material balance approach is feasible and may produce capture efficiency results of acceptable accuracy. However, previous limited testing has not produced conclusive results either negative or positive, and most tests were not designed as liquid/gas material balances.

Determinations of capture efficiency by this method are heavily affected by any variance of values within the equation, which are in turn impacted by the measurement of the individual test parameters. A number of sources potentially causing inaccuracies in liquid and gas measurements have been outlined in the previous section. Each of these potential sources is considered correctable to some degree. Short term testing under non-steady

state conditions, however, appears to compound these variances. Both short term testing under steady state conditions and long term testing under non-steady state conditions appear to be potentially feasible in producing acceptable results. The steady state conditions during short term tests tend to reduce any drastic stream fluctuations which might not be detected or which might create less accurate measurements. The longer test periods, where non-steady state conditions are encountered, tend to provide a greater averaging period for measurements thus reducing the impact of measurement variability under fluctuating conditions.

There is one additional limitation of the liquid/gas-phase approach, which also affects all methods requiring the measurement of the captured gas stream (e.g. gas-phase approach). It cannot be applied to operations employing direct fired ovens (which destroy a portion of the VOC), where the oven is in line with the capture stream and is located upstream of the first accessible measurement point on the capture stream. In this case, a material balance determination of capture efficiency using capture stream measurements is technically infeasible because some of the VOC is destroyed prior to reaching the measurement location.

## 3.2 REVIEW OF TRACER CONCEPTS

Three general classes of tracers were considered: (1) liquid tracers, (2) gaseous tracers, and (3) aerosol tracers. They are described and evaluated in the following paragraphs.

### 3.2.1 Liquid Tracers

Liquid tracer concept would make use of a unique volatile liquid having vaporization characteristics similar to the volatile components in the process being evaluated. The tracer would possess unique qualities allowing it to be detected accurately at low levels and to be distinguished from emissions emanating from adjacent operations not involved in the test. A known quantity of a volatile liquid tracer material (e.g. fluorocarbons, tagged or labeled compounds, or radioisotopes) would be injected into the coating and allowed to disperse. The gaseous tracer mass would then be measured in the capture stream during the test period and compared to the mass of the injected liquid tracer material, following procedures similar to a liquid/gas-phase material balance.

#### 3.2.1.1 Evaluation of Methods--

The liquid tracer approach was conceptualized during this study and, as far as could be determined through a literature search and other direct contacts, it has not been previously attempted or evaluated for quantitative determinations.

Because of the similarity of this method to the liquid/gas material balance, it would inherit the same difficulties and possible sources of variance. The only obvious advantage is that this method would distinguish between the emissions from the test source and those from adjacent non-test sources.

Stable tagged or labeled compounds were the only materials identified as likely candidates to be used as tracers. The use of these compounds would require custom compounding of liquids representing the properties of each solvent used throughout all coating industries. Stable labeled compounds would also require analysis by mass spectrometry. Another concern with liquid tracers is that they may bond differently with the other coating components causing the tracer to release differently than the normal solvents.

3.2.1.2 Assessment of Feasibility--

The feasibility of this approach technically is questionable since it is unknown how the materials will react with the other coating components. From discussions with industry representatives, they would only be agreeable to injection of the foreign substance into the process if they are provided assurances that it will not affect the product quality.

Economically, the liquid tracer concept is considered infeasible because of the costs associated with custom compounding of tracers. Also, the cost of mass spectrometric analyses associated with stable labeled compounds will probably be cost prohibitive.

Finally, this approach would be more costly and difficult than a typical liquid/gas-phase material balance and would provide essentially the same results.

3.2.2 Gaseous Tracers

The gaseous tracer concept takes a different approach from that of the liquid tracers. Since the gas cannot by itself simulate the variable rate of vaporization of the volatile liquid organic material used, a two step approach is necessary: (1) determination of the efficiency with which emissions are captured from each major emission point and (2) determination of the VOC emission rate at each emission point or the relative contribution of each segment to the total emissions.

The first step requires that the tracer gas be released at the surface of each unenclosed emission point and the amount collected in the capture stream be measured. This comparison or determination of the hood capture efficiency might be accomplished by either of two methods. The first is an absolute mass balance determination, and the second is a relative determination.

In the absolute mass determination, a known mass of the tracer gas would be released at the emission point. The total mass of tracer passing through the capture stream would be measured as in a mass gas flow measurement. Then, the two masses would be compared to determine the capture efficiency.

In the relative determination, the tracer gas would be released at a constant rate and the discharge nozzle placed inside the capture system ducting to assure 100% capture. The capture stream direct reading monitor scale would be marked to reflect this detection level as 100%. A linear scale would then be established between 0 and the 100% level. The tracer gas would then be released at the same set calibration flow rate only at the surface of the

emission source this time. The capture stream monitor records the percentage captured relative to the calibrated scale.

The second step would be determination of the fractional emission contribution or the actual emission rate for each emission segment. This could either be based on generalized emission factors for emission source segments or components for each industry category or on site-specific determinations of emission factors or rates.

The final capture efficiency determination for the total source (entire coating line) would then be made by weighting the capture efficiencies for each emission source segment (e.g. the product of the fractional contribution and the average capture efficiency for each segment) and summing the weighted capture efficiencies.

3.2.2.1 Evaluation of Methodology--

Gaseous tracers, such as sulfur hexafluoride and radioisotopes, have been used rather extensively as tracer materials for air flow studies and to some degree in capture efficiency studies (10-15). Sulfur hexafluoride ($SF_6$) seems to be the gas of choice in most studies because of its low level of detection by electron capture, its inert characteristics, its thermal stability, and its low toxicity. $SF_6$ has typically been used in outside dispersion studies and air exchange or dilution studies indoors.

Only limited work has been conducted using $SF_6$ for quantitative determinations of capture efficiency (13, 14, 16). However, none of these studies has involved determination of capture efficiency for an overall process line comprised of multiple emission sources (e.g. open coating vessels, open coating pans, coated web flash off area, and coated web oven zone), each possessing a different emission rate and a different fractional contribution of the total emission. These studies have found that the use of $SF_6$ for determination of capture efficiency produces reliable results, when releasing the tracer gas at a fixed rate from various points along the emission source. They have not, however, determined a statistical basis for the methodology (e.g. the number of release points required to accurately characterize the average capture efficiency of a source) nor answered many other important questions required prior to the general application of this method. One minor concern with this method is the amount of time and effort that would be required to fully characterize all of the unenclosed emission segments with the capture system operating under the same conditions and influences (e.g. same flow rate and same similar web speeds).

The release of $SF_6$ at a constant rate and the measurement of relative responses in the capture stream seems to have several advantages over the method requiring an absolute mass comparison. It only requires measurement and recording the relative responses detected in the capture stream when the tracer reaches steady state flow conditions, while the second method requires determination of flow and concentration of both the gas release stream and capture stream with time and full integration of the measured results. Therefore, the potential sources of error and the time per test are reduced. The determination of relative responses also should negate any effect of

reactivity (chemical or thermal) which might occur. It is likely that this type of test might also be applicable to process lines involving direct fired or zone incinerated ovens, where the captured gas stream cannot be measured before the oven.

In order for this test method to be applied to capture efficiency as it pertains to NSPSs for surface coating operations, emission factors (relative or absolute) must be known for each source segment (e.g. coater and oven). Industry representatives contacted were unaware of any existing data characterizing the emissions from different source segments. NSPS background information documents for some coating industries (e.g. metal coil coating) do contain some very general emission factors or ranges of factors for the major emission segments.

There are two possible approaches to defining emission factors for each source segment. The first is a general approach of developing emission factors for emission source segments within each industry category. The second is a direct approach of determining the emission factors for each site based on the site specific conditions.

In the general approach, the emission factors could simply be determined based on industry wide measurements of emissions contributed by the type of source. These general emission factors would be determined on a one time basis and would be applied to all plants within that industry category or within individual subsets of an industry category. The obvious disadvantage of such an approach is that it would provide a very broad approximation of actual emissions where significant changes could occur from one line to another or from one process to another due to many variables including solvent type, line speed, and coating thickness.

The second approach, development of emission factors at the test site, would provide emission factors based on the site specific operations and configurations. Two techniques for determining site specific emission factors have been considered: (1) direct measurement of emission levels or relative emission levels at different points on each source segment and (2) development of emission factors per unit of exposed surface area for the specific coating material being used and for the conditions under which it is being used (e.g. temperature, velocity, and humidity). The applicability of the first technique was evaluated during site visits at various surface coating plants during this study and was found unacceptable. Attempts were made to determine relative emissions from different points along the process line by conducting measurements of VOC concentration and velocity using direct reading instruments (e.g. TLV Sniffer® and velometers). In the cases evaluated, the measurements of concentration and velocity were generally unstable and inaccurate, and the emission surfaces along the web were often difficult to access. The feasibility of the second technique was not fully evaluated during this phase and was only conceptualized. This technique might involve the use of a small evaporation test chamber and a sample of the liquid coating material being used in the process. The test chamber could be used either in the field or at a laboratory. Emission data could be developed in terms of mass of VOC emitted per unit surface area of liquid coating per period of time. Test data of this

type could be developed using a test chamber for each type of coating or solvent mixture and plotted against varied conditions (e.g. temperature, velocity, and pressure). This type of data would not be applicable to curing surfaces (e.g. drying web); however, the drying web is located inside a totally enclosed oven.

The overall advantages of the gaseous tracer measurement concept are that: (1) it could provide a quantitative value of capture efficiency on any coating line (including those with zone incinerated or direct fired ovens), (2) it would not require the installation of a temporary test enclosure, and (3) the test could be conducted independent of the length or steady state characteristics of the process being tested. The potential disadvantages are the unknown length of time that would be required to make the test (especially if detailed emission factors must be determined) and the unproven methods being considered.

3.2.2.2 Assessment of Feasibility--

Based on the review conducted, the use of tracer gases to determine capture efficiency might be a feasible approach. However, the potential applicability of this approach would be heavily dependent on the development of acceptable emission factors or methods for determining emissions for each emission source. The use of $SF_6$ tracer gas for measuring the capture efficiency of a single hood has been demonstrated in research by other groups for other purposes. It would certainly require some further development or refinement before it could be applied to the testing of a process line for compliance determination purposes.

This method is not envisioned as a potential replacement for the direct material balance techniques, where they are feasible. However, the tracer gas method might provide an option to constructing an enclosure if the method could be developed. If so, it might provide a test method for determining capture efficiency on process lines utilizing zone incinerated or direct fired ovens.

3.2.3 Aerosol Tracers

The aerosol tracer concept follows an approach identical to that of the gaseous tracers. The only difference in the approaches is the release of an aerosol rather than a gas. Therefore, no further description is provided here of the method or procedures.

3.2.3.1 Evaluation of Methodology--

Aerosols used as tracers (e.g., uranine dye and ammonium chloride) have also received substantial attention in the past for air flow testing. Many of the reported tests and uses have involved dispersion testing or other ambient air flow problems. Of the material reviewed, only one source discussed using aerosol tracers to determine capture efficiency on exhaust hoods (17).

Although the aerosol tracer concept is similar to the gaseous tracer concept and has many of the same advantages and disadvantages, it has a distinct disadvantage associated with closed flow systems. Deposition of the aerosol can occur on surfaces contacted (17). With the number of turns and

other potential deposition surfaces that would be encountered prior to measurement in capture systems, the measurements may be reduced in accuracy.

There is also the underlying concern that an aerosol will not behave in flow identically to VOC gases or vapors. This is not believed to be a major factor because of the disperse nature of the aerosols that would be used.

3.2.3.2 Assessment of Feasibility--

The use of aerosol tracers is considered potentially feasible. However, there is no apparent advantage and several disadvantages in comparison with the use of tracer gases.

## 3.3 REVIEW OF MODELING CONCEPTS

The modeling approach assumes the use of a code (model) that, when input with the required conditional data, will define the capture efficiency of VOC emissions under the given emission, control, and site conditions through the use of a computer simulation. In order to represent capture efficiency as defined in this study and some NSPSs, codes are required to describe two separate activities which interact. These two activities are: (1) the formation of induced air flow patterns in and around the exhaust hoods and process line and (2) the evolution and mobility of process VOC emissions.

Once the computer code or program is selected, the model can be applied to determine capture efficiency by conducting a site visit to collect the conditional input data.

### 3.3.1 Evaluation of Methodology

A review of available literature and contacts uncovered no existing models specifically designed to meet the needs of this project. Most existing models addressing the mobility of airborne masses are related to activity in the outdoor ambient atmosphere and not the complex internal atmosphere of an industrial plant. Additionally, there are no known models describing the movement of air in three dimensions around exhaust openings of varying geometry, nor has the theory of industrial ventilation been developed to address capture efficiency as defined in this study. Therefore, this approach would require the development of new models.

Model development would have to take into account every variable which could possibly affect the capture system flow patterns, VOC evolution, and mobility of the emitted vapor. The National Institute for Occupational Safety and Health (NIOSH) considered development of such models several years ago but quickly abandoned the idea when the required degree of effort was evaluated.

If models were developed to depict the activities described, the combined model must be verified or adjusted before it could be legitimately applied. This process would require a significant amount of field testing to statistically validate the model. The field testing activities would have to be conducted by valid and accepted methods, which at this time is limited to the gas-phase material balance methods.

Because of the large number of affecting variables that would change from operation to operation and plant to plant, the field task for gathering input data would still be significant in order to apply the model. The amount of time required to collect input data tends to reduce the intended efficiency of the model approach. The types of data and measurements that may be required from each plant site include:

- types of solvent used and their characteristics,
- surface area of product throughput as a function of time,
- product throughput speed,
- type of applicator (e.g. spray or roll),
- application rate,
- surface area of applicator and reservoir exposed to the atmosphere,
- length of the process line (or product) through each segment,
- surface temperature of the emission source at each segment of the process line,
- velocity of any extraneous air currents (e.g. makeput air or dryer air) impinging on the coated product and the particular surface of the product impinged,
- location, configuration and dimensions of each hood (including all openings),
- location, configuration, and dimensions of all air flow obstructions,
- volumetric flow rate through each exhaust hood,
- portions of the process enclosed by any exhausted enclosure,
- velocities and area of influence of any other external air currents within the process area but not impinging on the coated product, and
- relative location of each emission source surface with respect to each exhaust point (three dimensional coordinates).

### 3.3.2 Assessment of Feasibility

Theoretically, it appears that a model could be developed to represent capture efficiency. For modeling to be advantageous, it should require a field testing and analysis effort to develop input data, which would be no more rigorous than that required for direct test methods. The effort that would be required to develop and verify an accurate model, based on all of the potentially affecting variables, would probably be much greater than that required to directly measure the capture efficiency of all new sources. There seems to be no apparent advantage to this approach.

## 3.4 REVIEW OF APPROXIMATION OR ASSUMPTION CONCEPTS

Assumption concepts would involve the use of logical assumptions and non-quantitative methods to conservatively approximate the capture efficiency. This type of approach may make use of visible chemical smoke. The smoke could be used to visibly demonstrate capture and control of emission source segments of the operation, which are exhausted by partial enclosures or external hoods to the control device. Source segments of the process would include coating feed tanks, coating applicators, the web flashoff area, and the dryer.

In this approach, smoke would be released at the surface of the emission source segment or released at openings on a partial enclosure around a segment.

If the smoke is visibly observed to be drawn entirely into the capture and control system, then the segment may be considered totally controlled. In the case where all emission source segments are visually demonstrated to be controlled, the capture efficiency may be assumed to be 100% or equivalent to a total enclosure.

In cases where total control is demonstrated only on certain source segments and not the entire operation, an "all or nothing" approach might be used, whereby only totally controlled segments are given credit as being captured. To obtain a quantitative capture efficiency value for the entire operation, the relative significance of each totally controlled emission source segment to the total operational emissions would have to be defined. The overall capture efficiency would be determined by summing the percentage contributions of each controlled source segment, as shown in the following hypothetical example:

| Emission Source Segment | Emission Contribution | Controlled (Yes/No) | Total Emissions Controlled |
|---|---|---|---|
| Coating Reservoir | 2% | No | 0% |
| Coating Pan/Applicator | 5% | No | 0% |
| Web Flash-Off | 8% | Yes | 8% |
| Dryer/Oven | 85% | Yes | 85% |
| TOTAL | 100% | | 93% |

### 3.4.1 Evaluation of Methodology

The use of this approach was conceptualized in this study and was not reported in the literature. However, the use of smoke tubes is a common inexpensive practice to evaluate the performance of air movement and collection systems.

Smoke tubes can be used to effectively assess the total control of emissions from a given point. Smoke tubes were used successfully to observe capture of emissions at numerous plants visited in a variety of surface coating industries. There were concerns among only a few plant representatives initially that the acid base smoke might affect the product quality if used near the web. However, the smoke was used with their cooperation in the vicinity of the product in all plants with no problems. The density of the smoke does not necessarily represent the density of saturated solvent laden air, but in spaces normally occupied by workers the air movement is great enough to control employee exposures and the solvent laden air is quickly diluted and approaches the density of clean air at ambient conditions.

The application of the assumption concept appears fairly straightforward in the determination of total operation control and could be easily implemented to demonstrate total control, where applicable. Where only certain source segments are totally controlled, there would be a requirement to develop emission factors for each specific coating operation and source segment.

### 3.4.2 Assessment of Feasibility

These conceptualized methods are viewed as feasible, particularly as a screening technique for total control. Based on the conservative estimates of capture efficiency that might be obtained at partially controlled operations, the costs associated with the development of emission factors may not be warranted. However, if emission factors are developed as an integral part of the tracer gas methodology, smoke tubes and the assumption concept may be used effectively as a screening technique before deciding to test with the more expensive tracer gas technique.

## 3.5 SELECTION OF A PREFERRED METHOD

Several test concepts or methods were found feasible based on the reviews in the previous sections. However, no single method was fully developed nor applicable to all possible test conditions and scenarios. Therefore, the selection of a single preferred method to receive further testing was made difficult.

The liquid/gas-phase material balance approach was selected as the preferred methodology based on the premise that direct measurements are more readily accepted for compliance demonstration than are indirect ones, and that material balance methods are generally further developed. Additionally, from the review it was concluded that the liquid/gas-phase approach had not received sufficient testing to conclusively evaluate the methods.

It was concluded that further testing of the liquid/gas-phase methodology was necessary to either validate or invalidate it as an acceptable alternative to the gas-phase approach. It was further concluded that this testing should be conducted in two steps: (1) laboratory testing and (2) field testing.

The laboratory studies (step 1) were considered necessary because of the complex array of measurement points, uncontrollable operational variables, and difficulty in measuring VOC fugitive losses and product retention at even the simplest field setting. It was stratigically important to begin testing under the simplest conditions and work up in complexity, and to be able to control and measure all streams for verification of test results. The laboratory allows both of these criteria to be met.

# SECTION 4

# LABORATORY TESTING

The objective of the laboratory experimental work was to assess the reliability of the available measurement methods in determining a liquid/gas-phase material balance under controlled laboratory conditions. The conclusion of this work is an assessment of the alternate methods and any limitations observed in the laboratory setting.

This section provides a description of the laboratory experimental approach, the experimental work (apparatus, procedures, and methods), test results, data quality, and conclusions.

## 4.1 EXPERIMENTAL APPROACH

From the review of the following subsection and the discussion of liquid/gas-phase material balances in Section 3 it should be obvious that field test conditions can be very complex. Even the simplest field test conditions are considered too complex of a setting to adequately assess the available measurement methods. Therefore, the laboratory tests were designed to allow a controlled evaluation of the available methods.

### 4.1.1 A Typical Liquid/Gas Material Balance

A liquid/gas material balance requires the measurement and comparison of the liquid VOC mass used at the coating operation and the gaseous VOC mass captured from the operation and sent to the control device. The capture efficiency is calculated as the percent ratio of captured VOC mass to liquid VOC used (vaporized) as presented earlier in Equation 2.

The mass of liquid VOC's entering the system during a material balance test period is determined by maintaining an inventory of the liquid usage and determining the VOC content of the liquids. The liquid use is typically determined by weighing aliquots, metering streams, or depth gauging tanks. The liquid input includes the addition of solvent for viscosity adjustment or wash solvents used during the test period. Measurement of the liquid VOC input in the field is often complicated by recirculating coating streams, multiple coaters on a single production line, lack of measurable streams in the coating area (e.g. the coating tank which feeds the coater is located in an area outside the test boundaries), and multiple coating lines (regulated and unregulated) sharing the same coating tank.

During the time that liquids are being processed, the flow rate and VOC concentration of the captured gas stream(s) are measured to determine the mass of captured VOC. The flow rate and concentration are monitored on a continuous or semicontinuous basis because of fluctuations that typically occur. Measurement of the captured VOC from the coating operation may be complicated by any of the following:

- poor flow measurement locations in a section where the flow profile is nonuniform,

- addition of VOC to the capture stream from operations or sources outside of the test area, or

- widely fluctuating gas stream conditions (concentration and flow) from process starts and stops or control adjustments.

4.1.2 Experimental Design

In order to effectively evaluate the performance of the analytical methodology, most of the variables experienced in the field were eliminated or strictly controlled during the laboratory testing. The test system was designed as a simple flow-through evaporation chamber, providing 100% capture and reducing the number of measurement parameters to the lowest possible state. Therefore, a known-capture efficiency was established for comparison with the measured and calculated values, and sources of error in measurement were reduced to the lowest level. Only field test variables that were easily simulated and controlled or that might directly affect the statistical evaluation of the methodology were allowed in the experimental design.

The experimental work was designed to evaluate specific test methods under a range of measurement conditions simulating some of the variable test conditions that might exist in the range of industries that could be tested. The experiments were designed to involve numerous test runs varying these conditions, while maintaining constant the measurement methods and the system configuration.

For practical purposes and the elimination of an additional set of test data required during the mass balance experiments, a separate set of experiments was designed to test the gas flow rate measurement methods. Therefore, the experimental work and design is divided into two separate but related investigations: (1) gas flow rate experiments and (2) mass balance (evaporation) experiments. The designs of these individual studies are further described in the following paragraphs.

4.1.2.1 Gas Flow Rate Experiments--

This study was designed specifically to assess the sensitivity of the gas flow rate determinations to various aspects of the velocity measurement methods. Some work has been done towards investigating the variability of the EPA method for gas flow rates which indicates sufficient precision for capture efficiency determination (18, 19). This study should conclude in determining the best procedure and circumstance to be used for all velocity traverses in the later laboratory and field studies.

Variations in pitot tube type, pressure measuring device type, operator, flow rate and sampling location were included in the study to determine their individual and combined effects on gas-phase flow rates.

The following is a listing of the variables and the specific levels selected for testing.

| Variable | Levels to be Tested |
|---|---|
| Pitot Tube | 2 (S-type and standard type) |
| Pressure Measurement Device | 2 (Magnehelic® and Inclined Manometer) |
| Flow Rate | 3 (20, 30, and 40 feet/second) |
| Traverse Location | 2 (Optimum and non-ideal) |
| Personnel | 3 (Field Test Engineer, Chemist, and Technician) |

The study was designed to utilize fractional factorial statistical techniques to investigate the precision of the flow rate mesurements. This type of design is advantageous where there are several variables affecting a measured parameter. For any test, the measured quantity is dependent on one or more variables, each of which can exist in one or more states. Thus, if X variables can have two possible states and Y factors can have three states, an investigation of all possible combinations would require $2^X \cdot 3^Y$ experimental runs. Through fractional factorial design techniques, it is possible to conduct only a portion of the possible experiments without sacrificing important information. The ability to estimate main effects and low order interactions of interest is retained. However, higher order interactions cannot be determined. Since high order interactions are somewhat unusual and often difficult to interpret, this sacrifice seems reasonable.

A full investigation would have required $2^3 \cdot 3^2$ or 72 individual traverses. Assuming that three factor and higher order interactions are negligible, the number of traverses was lowered to 36. Simultaneous measurements proved to be impractical. The test matrix is presented in Section 4.2 (Table 3).

4.1.2.2 Mass Balance (Evaporation) Experiments--

This set of laboratory experiments was designed to assess the reliability of the best available liquid and gas-phase measurement methods, and to evaluate their applicability in the determination of liquid/gas material balances.

The design of this investigation involved the testing and evaluation of the measurement methods as a set and in some cases on an individual basis. The set of measurement methods for liquid and gas parameters are ultimately evaluated on their ability to close the overall material balance. Where several potentially acceptable methods existed for the measurement of a given parameter, the tests were designed to conduct parallel measurements under the same test conditions in order to make a comparative evaluation of the individual methods. The bias involving the total set of measurements is strictly controlled by the design of rigorous quality control procedures for each individual measurement method employed.

The experimental test matrix was designed to evaluate the test methods under a range of measurement conditions simulating some of the test variables that might exist in the range of industries potentially tested. Numerous test runs were designed into the matrix in which the measurement conditions were varied, while maintaining the same system configuration and measurement methods. The variables and their designed test levels are:

| Variable | Levels to be Tested |
|---|---|
| Composition of Organics | 3 (pure solvent, binary mixture, commercial coating) |
| Mass Throughput of Organics | 3 (0.5, 1.0, 2.0 liters) |
| SLA flow rate | 3 (20, 30, 40 ft/second) |

A full investigation of all variables and their interactions would require well over 100 individual evaporation tests. By making simplifying assumptions and statistically evaluating the data, the number of tests was reduced. For instance, it was assumed that data from an experiment using only MEK would be equivalent in its contribution to the variability in a run using only toluene. A full test matrix is given in Section 4.2 (Table 4).

Each of the test variables is discussed below.

Composition of Organics--Surface coating operations cover a multitude of process environments. The variety of solvents and solvent mixtures used is very wide. However, two solvents, toluene and MEK, are in common usage throughout the industry.

These two VOCs were chosen to represent the solvents in coating liquids. Toluene (BP = 231°F), with a lower explosive limit (LEL) of 14,000 ppm and a specific vapor volume of 9.2 $ft^3/L$ was chosen as a less volatile compound than MEK (BP = 176°F), which has a specific vapor volume of 10.8 $ft^3/L$ and an LEL of 18,000 ppm. In addition to tests with pure solvent, mixtures of pure solvents and a commercial coating mix were tested.

The varied composition of organics in the liquid mixture or coating material primarily presented a test of the measurement methods for gas-phase VOC concentration.

Mass Throughput of Organics--In many plants, the surface coating operation is somewhat of a batch process and process runs vary in length. Changing coils or webs, product changes, and periodic equipment failures are some of the factors involved.

To simulate variability in the length of runs, the amount of liquid solvent placed in the evaporation chamber was varied from 0.5 to 2.0 liters. This variable may have an impact on all measurements because of the averaging effect associated with time.

It is anticipated that a VOC concentration versus time profile will produce a rapidly rising front area, a relatively stable center area, and finally, a slowly declining tail end. It is further anticipated that a plot of incremental solvent weight loss versus time will produce a similar curve. Under these circumstances, the data would provide knowledge of the relative contribution of the non-steady state conditions (both ends) to the overall uncertainty in the mass balance closure as the length of measuring time is varied.

For each experiment, the data from various time increments was to be examined separately from the data analysis of the entire run. Ultimately, the data may provide an estimate of the minimum testing time required for adequate characterization at actual plant sites under ideal conditions.

SLA Flow Rate--Throughout the industry, flow rates of the solvent laden air (SLA) vary depending on blower size, duct dimensions, and flammability characteristics of the solvent. The effects of SLA flow rate on mass balance closure are examined by testing at three SLA flow rates. Nominal values of 20, 30, and 40 ft/sec are selected. These represent typical flow rates found in surface coating plants.

In the laboratory studies the variation in flow rate will also affect the rate of vaporization and the dilution of the volatilized solvent, thus affecting the SLA concentration.

Liquid Organic Surface Area--For many of the plants involved in surface coating, the VOC concentration varies over a wide range. These variations arise from differences in substrate widths, substrate speeds, and coating thickness. In plant operations, this phenomena is independent of the other variables.

In the evaporation experiments, this variable was originally included in the design. However, this proved to be very impractical. With the relatively high SLA flow rates, severe swirling and choppiness developed on the surface of the VOCs. An airfoil was attached to the inlet chamber to prevent the VOCs from actually being swept out of the evaporation chamber and into the mixing chamber. Since this variable was not essential to the success of the study, it was dropped from the experimental design.

## 4.2 EXPERIMENTAL WORK

The experimental work accomplished in this study involved designing and building the test apparatus used in both of the laboratory experiments and conducting the gas flow rate and material balance experimental investigations. This section presents a description of the test apparatus and the experimental methods and procedures used in this work.

### 4.2.1 Test Apparatus

To satisfy the objectives of the experimental work, the test apparatus was designed to provide a simplified evaporation chamber with the ability to

simulate some field test conditions. The criteria for the design of this apparatus were:

- the ability to control and to condition the air flowing through the system,
- the ability to readily isolate the streams for mass balance determinations,
- the ability to contain all of the volatilized solvent from the point of solvent evaporation through the measurement points,
- accessibility of sampling points,
- accessibility of system components, and
- provisions for adequate safety.

A schematic representation of the apparatus used is given in Figure 2. This apparatus consisted of several segments described in the following subsections.

4.2.1.1 Air Inlet Chamber--

The air inlet was a rectangular box consisting of asbestos sheeting and measuring 12"W x 8"H x 24"L. A 12" x 12" sheet of 1/4" plexiglass was installed at the inside end of this chamber to control the air flow and minimize turbulence around the liquids contained in the evaporation chamber. Controlling the temperature and relative humidity of the incoming air were attempted but proved to be impractical due to the large air mass moving through the system. Thus, all experiments were designed to be conducted at ambient temperature and humidity.

4.2.1.2 Evaporation Chamber--

The air inlet chamber was followed by a detachable plexiglass chamber measuring 12"W x 11"H x 12"L. For all evaporation tests, a heated aluminum pan measuring 11 3/4"W x 2"H x 9 3/8"L was placed in the bottom of the chamber to receive the simulated coating mixture or solvent charges. The evaporation chamber rested on an analytical balance used to determine the mass of material in the system at any given time. Attachment of the evaporation chamber to the inlet and the mixing chambers was through flexible sheeting to minimize interference with the weight determinations.

Implicit in this design was the utilization of a total enclosure of the VOCs in the capture system. With fugitive losses held at essentially none, any discrepancies in the mass balance closures would be due to discrepancies within the analytical system.

4.2.1.3 Mixing Chamber--

After entering the gas-phase in the evaporation chamber, the SLA and air were allowed to mix and their turbulence decreased in a mixing chamber or plenum. This chamber consisted of a rectangular plexiglass box measuring

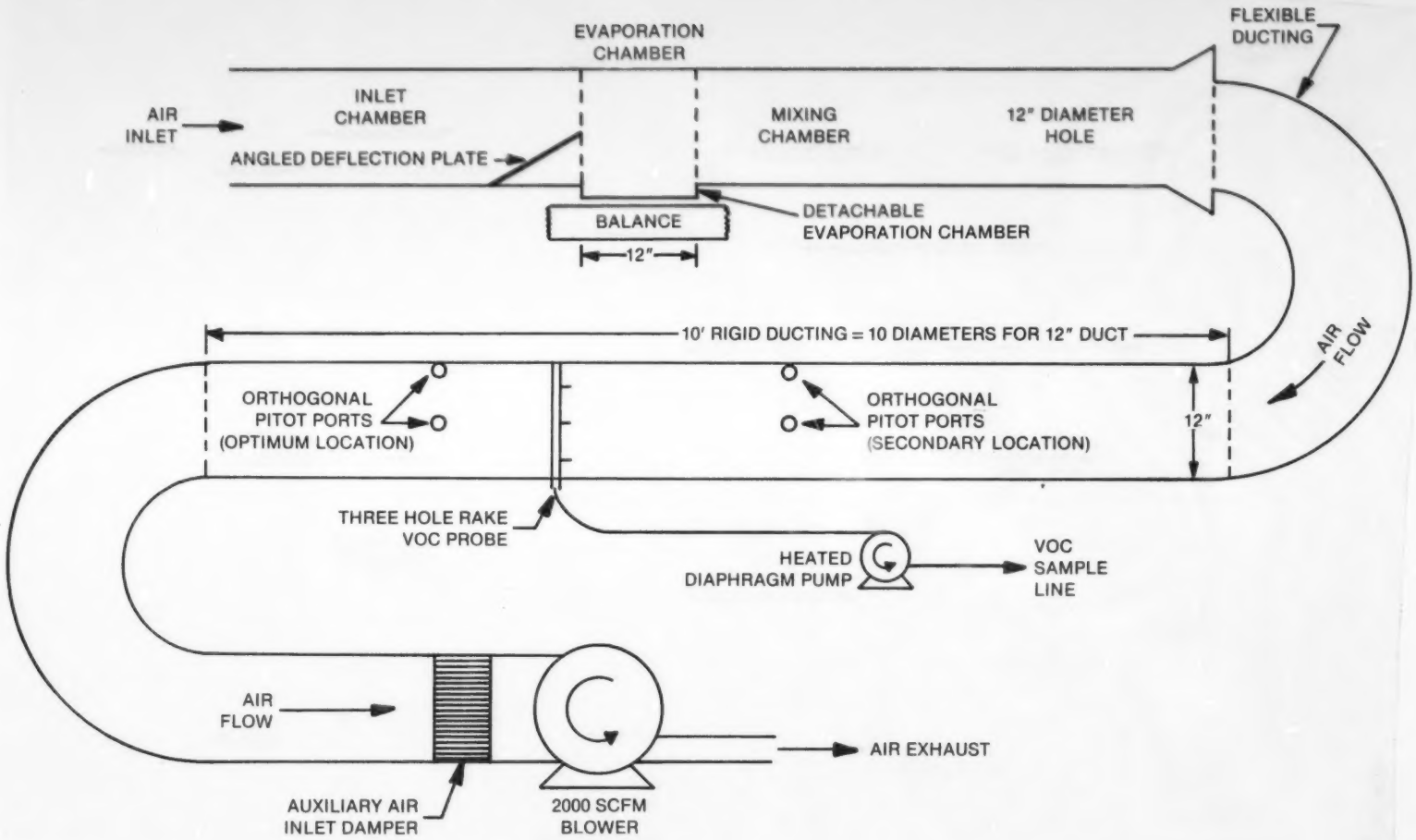


Figure 2. Test apparatus for capture efficiency laboratory study.

12"W x 9"H x 36"L. The exit end of this chamber was a round hole through which the main measuring duct extended.

4.2.1.4 Measuring Duct--

To ensure the applicability of the EPA reference method criteria for gas flow rate measurements, the measuring duct was designed of a round, rigid pipe, 12 inches in diameter and 120 inches long. To provide the measurement points (optimum and non-ideal) for the velocity traverses, two orthogonal holes were drilled at 24 inches from the exit end (optimum point) and two more at the midpoint in the length (non-ideal).

For collection of gas-phase samples to determine VOC concentrations a piece of 1/4 inch stainless steel tubing with 1/16 inch holes centered at 2.0 inches, 6.0 inches, and 10.0 inches was installed at a 45° angle and 12 inches upstream of the ideal velocity measurement ports. A slipstream sample of SLA was pulled continuously from the duct with a heated (400°C) diaphragm pump and analyzed for VOCs. The sample transfer lines were not heated since the entire system operated at ambient temperatures.

4.2.1.5 SLA Exhaust Blower--

All of the air through the entire system was drawn by a nominal 2000 SCFM blower attached to the end of the system. Air from the measuring duct was directed to the blower inlet through approximately 20 feet of 12 inch rigid ducting. A series of damper holes are cut into this ductwork to regulate the air flow rate through the test apparatus.

4.2.2 Test Procedures and Methods

The sampling and analytical methods used in this project are summarized in Table 2. Each is described in more detail in the sections following, which present the procedures and methods used in the individual investigations.

4.2.2.1 Gas Flow Rate Experiments--

In this investigation, thirty-six sets of gas flow mesurements were performed while varying the flow rate, the measurement location, the pitot tube type, the differential pressure measuring device, and the personnel. The test matrix presenting particular variables involved with each run is shown in Table 3.

EPA Method 2 was used as the standard method for conducting pitot traverses to measure differential pressure. This data when combined with stream pressure and composition, flow cross-sectional area, and static pressure yields a volumetric flow rate determination. Method 2 calls for 6 point traverses (per diameter) at the optimum locations and 8 point traverses at the non-ideal ports. The method does allow for measurements at additional traverse points if desired by the analyst.

All velocity traverses in this experimental work consisted of 9 point measurements. Eight were at locations specified by Method 2. The odd point was at the center of the duct. Data collected at this center point were not

TABLE 2. SUMMARY OF VOC CAPTURE EFFICIENCY SAMPLING/ANALYTICAL METHODS

| Measurement Parameter | Measurement Method(s) |
|---|---|
| Gas Velocity/Volumetric Flow Rate[a] | (1) EPA Methods 1 and 2 using an S-type pitot<br>(2) Traverses using a standard pitot<br>(3) Non-standard method using a continuous, center point pitot |
| Gas-Phase VOC Concentration | (1) EPA Method 25A (Byron 401 THC Analyzer)<br>(2) Draft EPA Method 18 (speciation using GC/FID)<br>(3) NIOSH Method 127 (charcoal tube absorption, $CS_2$ extraction, GC/FID analysis) |
| Liquid-Phase Mass | Direct Gravimetric Measurement |
| Liquid-Phase Volatile Content | EPA Method 24 |

[a]Temperature measured using type K thermocouples; since the sample gas consists primarily of air, a molecular weight of 29.0 will be assumed for flow rate calculations.

TABLE 3. TEST MATRIX FOR FLOW RATE INTERACTION EFFECTS

| Test No. | Pitot Tube Type | Pressure Measurement Device | Sampling Location | Nominal Flow Rate (ft/sec) | Personnel |
|---|---|---|---|---|---|
| 1 | S | Mag | NI | 20 | Chem |
| | Std | IM | | | |
| 2 | S | Mag | OPT | 30 | Tech |
| | Std | IM | | | |
| 3 | Std | Mag | OPT | 30 | Chem |
| | S | IM | | | |
| 4 | S | Mag | NI | 40 | Chem |
| | Std | IM | | | |
| 5 | Std | IM | OPT | 40 | Tech |
| | S | Mag | | | |
| 6 | Std | Mag | OPT | 20 | Tech |
| | S | IM | | | |
| 7 | S | IM | NI | 20 | Engr |
| | Std | Mag | | | |
| 8 | S | Mag | NI | 40 | Engr |
| | Std | IM | | | |
| 9 | Std | Mag | OPT | 40 | Engr |
| | S | IM | | | |
| 10 | Std | Mag | OPT | 20 | Chem |
| | S | IM | | | |
| 11 | S | IM | NI | 40 | Tech |
| | Std | Mag | | | |
| 12 | S | Mag | NI | 30 | Engr |
| | Std | IM | | | |
| 13 | S | Mag | NI | 20 | Tech |
| | Std | IM | | | |
| 14 | Std | IM | OPT | 20 | Engr |
| | S | Mag | | | |
| 15 | Std | Mag | OPT | 40 | Chem |
| | S | IM | | | |
| 16 | S | IM | NI | 30 | Chem |
| | Std | Mag | | | |
| 17 | S | Mag | NI | 30 | Chem |
| | Std | IM | | | |
| 18 | Std | Mag | OPT | 30 | Engr |
| | S | IM | | | |

Std = Standard pitot. S = S-type pitot
Mag = Magnehelic gauge. IM = inclined manometer
OPT = Optimum location (2 diameters upstream/8 diameters downstream).
NI = Non-ideal location (5 diameters upstream and downstream).
Chem = Chemist. Engr = Engineer. Tech = Technician.

used in calculating average differential pressure, but were collected to provide data for a single point reference.

Other miscellaneous measurements were made during the Method 2 type traverses. Temperature of the gas was measured with a K-type thermocouple and a calibrated digital read-out. Atmospheric pressure was determined by an aneroid barometer. The relative humidity was not measured, but the mole fraction of water in the gas stream was assumed to be zero. The dry molecular weight of the gas stream was assumed to be 29.0 g/g-mole as described in Section 3.6 of Method 2.

The tests were not necessarily conducted in the order shown in Table 3. Test runs were conducted in groups based on set flow rates in order to maintain a common condition for evaluation of the other variables.

4.2.2.2 Mass Balance (Evaporation) Experiments--

In this investigation, a series of twenty-four experimental runs was conducted using the best available liquid and gas measurement methods. The composition of organics, the mass throughput of organics, and the SLA flow rate were varied from one run to the next according to the experimental design and the resultant test matrix presented in Table 4.

In these experiments, a known quantity of liquid solvent or coating was placed in a pan located in the evaporation chamber, and the pan was heated to promote evaporation. Air was pulled through the system at discrete flow rates to produce an SLA flow through the measuring duct. While the known quantity of liquid solvent was being evaporated, the resulting VOC concentration and the flow rate of the SLA stream were monitored. Each of these measurements, including loss of liquid, was recorded at a corresponding frequency for incremental determination of mass balance closure. Each experimental run was terminated when the VOC concentration in the SLA stream fell below the background level.

Details of the procedures and methodology used in the measurement of each parameter are given below.

Gas-phase VOC concentration--Using the three-hole rake type probe, samples were collected from the SLA stream and analyzed for VOC concentration concurrently by different methods. These methods included EPA Method 25A, EPA Draft Method 18, and NIOSH Method 127. The first method uses flame ionization detection (FID) to provide total hydrocarbon (THC) concentrations. Similarly, the second method also uses an FID for quantitation. However, organic species in the sample are chromatographically separated prior to detection. The third method uses charcoal tube adsorption of VOCs followed by solvent extraction. The extract is analyzed by GC/FID.

EPA Method 25A and Draft Method 18 were utilized in each run of the experimental set, while NIOSH Method 127 samples were collected only on limited runs. The Method 25A measurements were made at one minute intervals. The Draft Method 18 measurements were conducted at seven minute intervals.

TABLE 4. TEST MATRIX FOR MASS BALANCE EXPERIMENTS

| Run No. | Organic Composition | Organic Throughput (Liters) | Nominal SLA Flow Rate (ft/sec) |
|---|---|---|---|
| 1 | MEK | 2 | 20 |
| 2 | Toluene | 0.5 | 30 |
| 3 | Toluene | 1 | 20 |
| 4 | Mixture[1] | 1 | 30 |
| 5 | MEK | 2 | 40 |
| 6 | MEK | 1 | 30 |
| 7 | Mixture[1] | 0.5 | 30 |
| 8 | Toluene | 2 | 30 |
| 9 | Mixture[1] | 0.5 | 20 |
| 10 | Mixture[1] | 1 | 40 |
| 11 | Mixture[1] | 1 | 20 |
| 12 | MEK | 0.5 | 40 |
| 13 | Mixture[1] | 2 | 30 |
| 14 | Toluene | 1 | 40 |
| 15 | MEK | 0.5 | 20 |
| 16 | Mixture[1] | 0.5 | 40 |
| 17 | Mixture[1] | 2 | 40 |
| 18 | Mixture[1] | 2 | 20 |
| 19 | MEK | 1 | 30 |
| 26A | Comm 1[2] | 1 | 30 |
| 22 | Comm 2[3] | 1 | 40 |
| 23 | Comm 2[3] | 1 | 20 |
| 26B | Comm 2[3] | 1 | 30 |
| 31 | Comm 3[4] | 1 | 40 |

[1] Mixture of 50% each by volume of MEK and toluene. Individual weights were used in the closure calculations.

[2] Commercial mixture of rubber in MEK, specified by the manufacturer to contain 31% solids by weight.

[3] Mixture described in 3 above diluted approximately 10:1 with MEK.

[4] Mixture described in 3 above diluted approximately 2:1 with MEK.

Method 25A specifies that THC determinations be performed using a continuous monitor equipped with an FID. Although an FID was used on this project, monitoring was performed on a semi-continuous basis using a Byron Model 401 THC analyzer connected to the VOC sampling manifold. The Byron 401 can be operated in one of two modes: THC or full scan. For this project, measurements were made only in the THC mode.

In the THC mode, sample is introduced continuously into a sample loop from the VOC manifold. At sample injection, the loop contents are flushed into a restrictor column (empty 1/16 inch tubing) and eventually flow into the detector. A complete cycle is completed in one minute. During each cycle, a built-in integrator is first cleared and then allowed to accumulate electrical charge corresponding to the detector response. At the completion of each analysis, this accumulated charge representing the integrated area is available for data recordation.

All data from the Byron instrument was automatically captured, stored on disk, and reduced using an Apple® II microcomputer. Software to accomplish this was tailored for this project. In addition, the computer recorded the date and time of analysis, instrument, analysis type, sampling location, and run number. As a backup to the microcomputer data acquisition system, integrated areas for the instrument were recorded using a strip chart recorder to provide hardcopy records of the analyses.

EPA Draft Method 18 differs from Method 25A in that sample acquisition may be performed either by direct interface or by grab sampling. In addition, the organic components of the stream are chromatographically separated prior to detection by FID. Sample gas for Method 18 was delivered via the multiport manifold, and analyzed concurrently with Method 25A analyses.

The instrument and analytical conditions used were:

- Instrument — AID Model 511
- Column — 18 in. x 1/8 o.d. s.s., Porapak Super Q, 80/100 mesh
- Carrier Gas — Nitrogen, approximately 40 mL/min
- Column Temperature — Isothermal at 170°C
- Injection — 5 mL fixed volume loop
- Integrator — Hewlett Packard Model 3390A

Gas from the VOC Manifold was flushed continuously through the sample loop. The injection valve was fitted with a Carle Model 4200 actuator controlled by an adjustable Eagle Signal timer. Cycle time was set at 7 minutes for all analyses.

The integrated areas from the integrator hardcopy were input manually to the Apple® II data acquisition system. This step was very helpful in reporting results on a consistent basis. Additionally, it facilitated simple statistical analysis of the data using computer techniques.

NIOSH Method 127 was followed in analyzing charcoal tube samples from selected experimental runs. However, sample collection deviated considerably from the methodology specified in Method 127.

Rather than use a personal pump calibrated with a typical tube, as specified in the method, each charcoal tube was attached directly to a line from the VOC manifold. Since this line was already pressurized from the heated diaphragm pump, a separate pump for the tube was not needed.

The exhaust end of the tube was directed into a Byron Model 90 mass flow meter/totalizer. This provided not only a continuous indication of flow rate, but also measured total air flow through the tube. The tube sample flow was adjusted for each run in an effort to provide maximum loading without breakthrough.

In the analysis step, the front section of the tube was desorbed with $CS_2$ for 1/2 hour. A 5 uL sample was then injected into a GC equipped with an FID. Instrumental and analytical conditions used were:

- Instrument — Varian Series 1400
- Column — 20 ft. x 1/8 o.d. s.s., 10% SP 1000 on Supelcoport, 80/100 mesh
- Carrier Gas — Nitrogen, approximately 25 mL/min
- Detector Temperature — 230°C
- Column Temperature — 60°C for 3 min. then 10°C per min. to 150°C, end at 20 min.
- Injection — 5 uL by syringe into port at 210°C
- Integrator — Hewlett-Packard Model 3390A

Since none of the front sections indicated extremely high loading levels, none of the back sections were analyzed.

Volumetric flow rate--SLA flow rates were measured at approximately midway through each run by EPA Method 2 without modification. An S-type pitot and inclined manometer were used to measure differential pressures. Details of these measurements and the other necessary data collection steps were described in Section 4.2.1. A complete traverse was performed during each evaporation run.

Additionally, the SLA flow rate was continuously monitored during each run with a standard pitot at the center of the non-ideal port. Differential pressure at this location was measured by a digital manometer and recorded on a strip chart recorder. The purpose for this step was to monitor any change in flow rate.

Mass of Liquid VOC--Determinations of VOC capture efficiencies require that the total mass of liquid VOC entering or existing in the system be known. For field operations, this is anticipated to be a formidable task. For the experiments, this task was relatively straightforward and simple.

Mass measurements were made on a calibrated laboratory balance capable of measuring to the nearest 0.1 g. The balance was permanently placed under the evaporation chamber to monitor the weight of the chamber and any liquid that it contains. During each evaporation run, an initial weight of liquid was recorded. Periodically, at 5 or 10 minute intervals, during the evaporation phase, instantaneous weights were recorded. The mass of solvent evaporated was determined by difference.

Verification of the mass of each liquid charge to the evaporation chamber was performed by weighing the solvent storage bottle before and after applying its contents.

In the tests involving pure solvents, i.e., no solids, virtually all of the solvent evaporates. In the tests involving a commercial coating mixture, the dissolved or suspended solids remained in the pan. For the laboratory tests, the solvent VOC weight loss was all that was required to perform a mass balance calculation. However, in the field where the solids completely disappear onto the web, the volatile content of the coating mixture will have to be determined, probably by EPA Method 24.

A brief examination of EPA Method 24 (ASTM Method D2369-81) was made on the commercial coating mixture used in the simulation tests. EPA Method 24 specifies that volatile content of coating mixtures be determined by running duplicate analyses using ASTM Method D2369-81 until the two values are within 1.5% of each other. The ASTM procedure is basically a weight loss on heating test. In the method, a discussion of precision indicates that a 60-minute heating period should provide a relative deviation of less than 1.5% at the 95% confidence level. A forced draft oven was used to minimize the possibility of a fire.

To perform Method 24 analysis, an accurately weighed sample (0.3 $\pm$0.1 g to the nearest 1 mg) was mixed with 3 mL of solvent for dispersion. This mixture was then heated for 60 minutes at 110 $\pm$5°C in the oven. The sample was then removed, cooled in a desiccator and reweighed. The weight loss was assumed to be the volatile content of the coating mix.

## 4.3 EXPERIMENTAL RESULTS AND DISCUSSION

The results of the laboratory tests are presented in this section for the separate series of experiments. The calculation methods and raw test measurement data are presented in Appendix C.

### 4.3.1 Gas Flow Rate Test Results

A fractional factorial designed series of experiments was conducted to evaluate the main and low order interaction effects surrounding EPA Method 2 type flow rate determinations. Thirty-six individual pitot traverses were performed to study the variability of flow rate measurements with pitot tube type, differential pressure measuring device, flow rate, personnel, and sampling location. Table 5 shows the variables studied, the level of each variable, and the results of the testing.

TABLE 5. TEST MATRIX AND RESULTS FOR FLOW RATE INTERACTION EFFECTS

| Test No. | Pitot Tube Type | Pressure Measurement Device | Sampling Location | Nominal Flow Rate (ft/sec) | Personnel | Velocity Measurement (ft/sec) |
|---|---|---|---|---|---|---|
| 1 | S | Mag | NI | 20 | Chem | 18.2 |
| | Std | IM | | | | 18.3 |
| 2 | S | Mag | OPT | 30 | Tech | 31.4 |
| | Std | IM | | | | 31.0 |
| 3 | Std | Mag | OPT | 30 | Chem | 32.0 |
| | S | IM | | | | 30.5 |
| 4 | S | Mag | NI | 40 | Chem | 37.1 |
| | Std | IM | | | | 38.8 |
| 5 | Std | IM | OPT | 40 | Tech | 40.1 |
| | S | Mag | | | | 37.0 |
| 6 | Std | Mag | OPT | 20 | Tech | 18.9 |
| | S | IM | | | | 17.3 |
| 7 | S | IM | NI | 20 | Engr | 18.8 |
| | Std | Mag | | | | 19.6 |
| 8 | S | Mag | NI | 40 | Engr | 38.1 |
| | Std | IM | | | | 39.3 |
| 9 | Std | Mag | OPT | 40 | Engr | 40.3 |
| | S | IM | | | | 39.2 |
| 10 | Std | Mag | OPT | 20 | Chem | 19.2 |
| | S | IM | | | | 18.4 |
| 11 | S | IM | NI | 40 | Tech | 39.2 |
| | Std | Mag | | | | 39.6 |
| 12 | S | Mag | NI | 30 | Engr | 32.0 |
| | Std | IM | | | | 31.5 |
| 13 | S | Mag | NI | 20 | Tech | 18.6 |
| | Std | IM | | | | 18.3 |
| 14 | Std | IM | OPT | 20 | Engr | 20.0 |
| | S | Mag | | | | 18.5 |
| 15 | Std | Mag | OPT | 40 | Chem | 39.7 |
| | S | IM | | | | 40.9 |
| 16 | S | IM | NI | 30 | Chem | 30.8 |
| | Std | Mag | | | | 31.4 |
| 17 | S | Mag | NI | 30 | Chem | 31.6 |
| | Std | IM | | | | 30.7 |
| 18 | Std | Mag | OPT | 30 | Engr | 31.5 |
| | S | IM | | | | 31.3 |

Std = Standard pitot. S = S-type pitot
Mag = Magnehelic gauge. IM = inclined manometer
OPT = Optimum location (2 diameters upstream/8 diameters downstream).
NI = Non-ideal location (5 diameters upstream and downstream).
Chem = Chemist. Engr = Engineer. Tech = Technician.

In the gas flow rate experiments, all test runs calling for a particular flow rate were conducted in sequence at the same setting with no change in the duct work or blower configuration. The velocity was set in the range of the specified level (e.g. 20, 30, or 40 feet per second) to produce data for a widely varied range of flow rates. Thus, the absolute values obtained for velocity are not as important as the relationship between grouped data for each velocity range setting.

Analysis of variance (ANOVA) techniques were used to test the statistical significance of first and second order effects from each of the variables. ANOVA is a statistical technique that separates the variations found within a data set into exclusive components and then tests various hypotheses about those components. A comprehensive discussion of ANOVA has been written by Cochran and Cox. (20) Results of the ANOVA study are presented in Table 6.

For the lowest flow rate, nominally 20 ft/sec, the type of pitot tube was found to affect the results. This was partly anticipated since the flow rate was near the lower limit of applicability for an S-type pitot. However, the significance level of $\alpha = 0.10$ indicates that the effect is only marginal, i.e., we are wrong in concluding a significant effect in 10% of the cases. Additionally, the relative difference between the two mean values is 4.0%.

For the middle flow rate tests, the type of pressure gauge was found to have a significant effect at the 0.05 level. It should be noted that the relative difference between the two mean values is only 2.2%.

For the highest flow rate, none of the individual variables was found to have a significant effect on flow rate measurements. However, through multiple comparison tests, the combination of S-type pitot and Magnehelic® gauge was found to provide different results at a significance level of 0.01. The relative difference between the mean for this combination and all other combinations is 8.1%.

For all data sets, the precision looks excellent. Coefficients of variation do not exceed 4%. The greatest variability is seen at the lowest flow rate where minor discrepancies in interpreting pressure gauge readings have a more pronounced effect. For instance, reading a value to the nearest 0.01 inch implies a potential error of 0.005 inch. If the correct value is 0.10 inch, the variability is $\pm$5%. However, if the correct value is 1.00 inch, then the variability is only $\pm$0.5%.

In the final analysis, it was concluded that no single variable or combination of variables provided distinctly better flow rate data. As a practical matter, this means that any combination of pitot tube, measuring device, personnel, and sampling location provides adequately precise flow rate measurements over the range studied.

TABLE 6. ANALYSIS OF GAS PHASE FLOW RATE TEST RESULTS

| Nominal Flow Rate (ft/sec) | Data | Mean--ft/sec (95% C.I.) | Number of Observations | Standard Deviation (ft/sec) | Coefficient of Variation (%) | Probability Level for Significance* |
|---|---|---|---|---|---|---|
| 20 | S-Type Pitot | 18.30 (17.74, 18.86) | 6 | 0.53 | 2.89 | |
| | Standard Pitot | 19.05 (18.33, 19.77) | 6 | 0.69 | 3.62 | 0.10 |
| | Overall | 18.68 (18.24, 19.12) | 12 | 0.70 | 3.77 | |
| 30 | Inclined Manometer | 30.97 (30.57, 31.36) | 6 | 0.38 | 1.22 | |
| | Magnehelic® Gauge | 31.65 (31.36, 31.94) | 6 | 0.28 | 0.89 | 0.05 |
| | Overall | 31.31 (31.01, 31.61) | 12 | 0.48 | 1.53 | |
| 40 | S-Type Pitot/ Magnehelic® Gauge | 37.40 (35.89, 38.91) | 3 | 0.61 | 1.63 | 0.01 |
| | Otherwise | 39.68 (39.18, 40.18) | 9 | 0.66 | 1.65 | |
| | Overall | 39.11 (39.43, 39.79) | 12 | 1.07 | 2.74 | |

* If this probability is small, i.e., 0.05, then you are wrong in concluding a significant effect only 5% of the time.

### 4.3.2 Mass Balance (Evaporation) Test Results

For this study, variations in solvent type, solvent amount, and SLA flow rate were designed to represent an adequate compromise between expected field conditions and the limitations of bench-scale testing. In order to reduce the number of tests and facilitate the analysis of the data, it was assumed that the data from one pure solvent is equivalent to the data from another pure solvent. This assumption was evaluated from the data collected and found to be correct.

A series of 19 experiments was conducted wherein known quantities of pure solvent were evaporated while the resulting VOC concentration and the flow rate of the SLA were monitored. These were conducted using MEK, toluene, and a 50/50 by volume mixture of the two.

An additional five experiments were conducted using a commercial coating mixture containing rubber dissolved in MEK. The initial test using this mixture as received proved unsatisfactory due to a crusting effect. To alleviate this problem, the other runs were made on a portion of the mixture diluted with MEK.

Liquid/gas closure values were independently obtained for each VOC measurement type (Method 25A, Method 18, and NIOSH Method 127). These are presented for each run in Table 7. The data were analyzed using techniques similar to those used for the flow rate study. To test the statistical significance of main and interaction effects, ANOVA methods were used. The results of this are given in Table 8. The results of each method are discussed in the following subsections.

#### 4.3.2.1 Method 25A Closure Results--

The Byron 401 analyzer was calibrated daily with certified gas standards containing MEK and toluene. Response factors were obtained for each compound and used to calculate concentrations in the SLA stream. For those experiments where the 50/50 mixture was used, an average of the two RF values was used to calculate concentrations.

A sample calculation showing conversion of the VOC concentration to mass of solvent is given in Appendix C. This calculation takes into account the SLA flow rate and utilizes temperature and pressure corrections. The total mass thus obtained was then compared to the weight loss measured with the balance under the evaporation chamber.

Mass balance closures were calculated for the individual time increments and for the total time elapsed interval, as shown in the sample calculations in Appendix C. Additionally, total mass balance closures were calculated from comparison of the initial solvent weight with the total sum of the measured VOC weights. Table 7 summarizes the conditions and both THC closure values for all of the runs. Also included in the table is similar information from the speciated GC-FID analyzer and charcoal tube analyses.

TABLE 7. LIQUID/GAS MASS BALANCE CLOSURES

| Run No. | Elapsed Time[1] (min) | Solvent Type | Solvent Amount (liters) | Measured SLA Flow Rate[2] (SCFM) | THC Closures | | Method 18 Closures | | | NIOSH 127 Closures | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Aggregate[3] (%) | Total[4] (%) | MEK (%) | Toluene (%) | Total[5] (%) | MEK (%) | Toluene (%) | Total[5] (%) |
| 1 | 100 | MEK | 2 | 832 | 100 | 100 | 73.0 | -- | 73.0 | 397 | -- | 397 |
| 2 | 56 | Toluene | 0.5 | 1400 | 101 | 101 | -- | 98.0 | 98.0 | -- | 210 | 210 |
| 3 | 140 | Toluene | 1 | 843 | 98.0 | 96.1 | -- | 88.5 | 88.5 | -- | 235[6] | 235 |
| 4 | 61 | Mixture[7] | 1 | 1417 | 107 | 108 | 84.7 | 106 | 95.3 | 90.1 | 216 | 153 |
| 5 | 86 | MEK | 2 | 1825 | 88.5 | 88.5 | 103 | -- | 103 | 117 | -- | 117 |
| 6 | 51 | MEK | 1 | 1471 | 109 | 107 | 88.5 | -- | 88.5 | NM | -- | NM[8] |
| 7 | 53 | Mixture[7] | 0.5 | 1395 | 93.5 | 100 | 103 | 156 | 129 | NM | NM | NM |
| 8 | 150 | Toluene | 2 | 1406 | 98.0 | 99.0 | -- | 119 | 119 | -- | NM | NM |
| 9 | 70 | Mixture[7] | 0.5 | 844 | 90.1 | 89.3 | 75.8 | 90.1 | 82.9 | 69.0 | 155 | 112 |
| 10 | 70 | Mixture[7] | 1 | 1753 | 110 | 110 | 174 | 546 | 360 | NM | NM | NM |
| 11 | 105 | Mixture[7] | 1 | 918 | 102 | 101 | 78.7 | 97.1 | 87.9 | 123 | 204 | 163 |
| 12 | 35 | MEK | 0.5 | 1718 | 98.0 | 100 | 76.9 | -- | 76.9 | 45.2 | -- | 45.2 |
| 13 | 81 | Mixture[7] | 2 | 1461 | 102 | 100 | 84.7 | 95.2 | 89.9 | 131 | 350[6] | 240 |
| 14 | 77 | Toluene | 1 | 1700 | 96.1 | 95.2 | -- | 87.0 | 87.0 | -- | 111 | 111 |
| 15 | 56 | MEK | 0.5 | 844 | 93.9 | 103 | 92.6 | -- | 92.6 | NM | -- | NM |
| 16 | 49 | Mixture[7] | 0.5 | 1787 | 99.4 | 100 | 96.1 | 95.2 | 95.6 | 50 | 149 | 99.5 |
| 17 | 60 | Mixture[7] | 2 | 1771 | 98.0 | 102 | 90.9 | 61.3 | 76.1 | 122 | 290 | 206 |
| 18 | 175 | Mixture[7] | 2 | 859 | 104 | 95.2 | 76.3 | 89.3 | 82.8 | 403 | 369 | 386 |
| 19 | 50 | MEK | 1 | 1834 | 100 | 107 | 77.5 | -- | 77.5 | NM | -- | NM |
| 26A | 156 | Comm 1[9] | 1 | 1411 | 119 | ND[10] | 90.1 | -- | 90.1 | NM | -- | NM |
| 22 | 190 | Comm 2[11] | 1 | 1769 | 93.5 | ND | 117 | -- | 117 | NM | -- | NM |
| 23 | 121 | Comm 2[11] | 1 | 922 | 99.0 | ND | 86.2 | -- | 86.2 | 118 | -- | 118 |
| 26B | 120 | Comm 2[11] | 1 | 1427 | 104 | ND | 98.0 | -- | 98.0 | NM | -- | NM |
| 31 | 241 | Comm 3[12] | 1 | 1730 | 99.0 | ND | 186 | -- | 186 | NM | -- | NM |

1. Elapsed time for each analysis varied due to cycle time and sensitivity differences.
2. Flow rate measured by EPA Method 2 during each run. (SCFM 47.124 X feet per second.)
3. Calculated from ( MW x 100/ CW) where MW = sum of the balance weight losses and CW = sum of the weight losses from the VOC concentration and the SLA flow rate. For the commercial mixtures, MW is the difference between the initial and final balance weights.
4. Calculated from (TW x 100/ CW) where TW is the initial total weight of solvent placed in the system.
5. These data are the arithmetic average of the MEK and toluene closures.
6. Average value of duplicate determinations.
7. Mixture of 50% each by volume of MEK and toluene. Individual weights were used in the closure calculations.
8. NM = not measured.
9. Commercial mixture of rubber in MEK, specified by the manufacturer to contain 31% solids by weight.
10. ND = not determined since all of the material was not evaporated.
11. Mixture described in 9 above diluted approximately 10:1 with MEK.
12. Mixture described in 9 above diluted approximately 2:1 with MEK.

TABLE 8. ANALYSIS OF MASS BALANCE TEST RESULTS

| Analysis Type | Data Type | Mean of Closures (%) | 95% Confidence Interval (%-%) | Number of Observations | Standard Deviation (%) | Coefficient of Variation (%) |
|---|---|---|---|---|---|---|
| EPA Method 25A/Byron 401 THC Analysis | Pure solvent (overall) | 99.9 | 97.1 - 102.7 | 19 | 5.9 | 5.9 |
| | Commercial mix (overall) | 102.2 | 89.6 - 114.9 | 5 | 9.1 | 8.9 |
| EPA Method 18/GC-FID with Speciation | Pure solvent (overall) | 105.4 | 75.0 - 135.9 | 19 | 63.9 | 60.0 |
| | Commercial mix (overall) | 115.5 | 64.4 - 166.7 | 5 | 41.2 | 35.7 |
| NIOSH Method 127/Charcoal Tubes | Pure solvent (overall) | 190.4 | 126.1 - 254.6 | 13 | 106.2 | 55.8 |

From Table 8, the only variable found to have a statistically significant effect on THC closures was the solvent amount, with a probability level of 0.10. As a practical matter, this marginally significant effect would be difficult to explain since the mid-level (1.0 liter) results seem to deviate from the low and high level results. Thus, none of the variables nor combination of variables seem to have any great effect on the closure technique results.

Accuracy, bias, and precision were evaluated for the pure solvent and the commercial mixture experiments as separate groups. Accuracy seems more than adequate for each group since the mean closure values are 99.9 and 102.2%. Bias is not indicated for either group since 100% is included within the 95% confidence interval in both cases. Precision or variability estimates for the two groups are excellent since the coefficients of variation are 5.9 and 8.9%.

Finally, the statistical evaluation indicates that the mass balance method using EPA Method 25A for VOC concentrations is adequate for VOC capture efficiency determinations at surface coating operations. Further discussion concerning accuracy and testing requirements will be given in following sections.

4.3.2.2 Method 18 Closure Results--

The Method 18 closure values are shown in Table 7. Separately measured solvent masses for the SLA stream were calculated in a manner analogous to that described for THC measurements. A sample calculation appears in Appendix C. Since the evaporated weight loss data were obtained at five- (in some cases ten-) minute intervals, and the SLA weight measurements were obtained every seven minutes, direct comparison of the masses could be made only at 35- or 75-minute intervals. As indicated by the elapsed time column of Table 7, most of the runs would include only one or two such comparisons. Thus, only total weights were used in the Method 18 closure calculations. The overall closures for mixture runs are the average between the separate MEK and toluene values.

From Table 8, there is not sufficient evidence to indicate significant main or interaction effect in the Method 18 closure results, at least to the 0.10 level. This may be due, in part, to the rather large variability associated with the method itself.

As with the Method 25A data, accuracy, bias, and precision were evaluated for the pure solvent and the commercial mixture experiments as separate groups. With mean closure values of 105.4% and 115.5% for the pure solvent and the commercial mixture tests, respectively, the method appears to be marginally accurate. The wide 95% confidence intervals (75.0 to 135.9% and 64.4 to 166.7%) tend to eliminate bias as a potential problem. However, the variability estimates as measured by the coefficient of variation indicate that the particular methodology used is not adequate for measuring capture efficiencies. This problem was verified by the QC activities which are further discussed in this section. While no actual cause of this inadequacy was determined, two major possibilities were postulated.

The first possibility involves variability in stream VOC concentrations and the measurement frequency used. A detailed review of the THC concentrations measured using Method 25A for each run shows variations with substantial up and down swings. These data, taken at 1-minute intervals, seem to have adequately followed these variations. The 7-minute interval data obtained by the Method 18 analyzer very likely missed a number of the peaks and/or valleys. This factor may have played a major role because of the relatively short test run periods.

During some of the runs, it was apparent that the sensitivity of the Method 18 analyzer changed during the run. This effect was particularly evident during Run Number 10 where the MEK concentration for the third sample had dropped to 26 ppm. At that point, the analyzer's detector jet was mechanically cleaned of a white powder which had collected on it. As evidenced by the data, sensitivity rose dramatically. The overall results show an excessive lack of recovery of the evaporated solvents. The extent of this problem was not quantified for any of the runs.

The GC/FID analyzer was operated at maximum sensitivity during each of the runs. Additionally, a rather large (5 mL) sample loop was used to obtain a relatively low detection limit. It is very possible that a more sophisticated or sensitive GC/FID instrument could provide better results.

This sensitivity problem could possibly have been quantified by following the dictates of the draft method, i.e., analyzing a standard after every three samples. However, this would certainly have exaggerated the effects of the first problem associated with the frequency of sampling.

4.3.2.3 NIOSH Method 127 (Charcoal Tube) Results--

Closure values for the charcoal tube samples taken during some test runs are given in Table 7. Individual VOC masses were calculated from the desorbed solvent mass and the ratio of sampled SLA to the total SLA flow. A sample calculation is given in Appendix C.

Full statistical analysis was not performed on the charcoal tube data. However, the data shown in Table 7 indicate that the method is not sufficiently accurate for performance testing. The most serious problem associated with this method seems to be its variability. As measured by the coefficient of variation, this was 55.8%. Some of the more obvious potential sources of this variability are discussed below.

Errors in charcoal tube flow rates do not seem likely since they would cause a bias in the results. The high recoveries indicated by the toluene results could support this type of error. However, the mixed high and low recoveries for MEK seem to eliminate it.

Duplicate analyses as well as other quality control efforts indicate that the problem does not lie with the laboratory analysis. A summary of the QC data is presented in Section 4.4.

Severe problems in the adsorption/desorption stage are indicated by the results obtained for Runs 3 and 13. The closure value of 235% for Run 3 is the result of averaging values of 358% and 112%. For Run 13, the MEK value of 131% came from averaging values of 240% and 22.3%, while the 350% closure for toluene was derived from 571% and 129%. In both runs, the tube samples were taken side-by-side from the same VOC sample line.

### 4.3.3 Volatile Content of Coating Mixture (EPA Method 24) Results

A brief examination of EPA Method 24 for determination of volatile content was made on three of the commercial coating mixtures. The samples were:

Comm 1 - mixture of rubber in MEK which contained 31% by weight of solids,

Comm 2 - an approximately 10 to 1 dilution of Comm 1 with MEK, and

Comm 3 - an approximately 2 to 1 dilution of Comm 1 with MEK.

Attempts to obtain the specified 0.3 mL of sample for Comm 1 failed. The material was simply too viscous to pull up into a syringe.

Obtaining a sample of Comm 3 was possible, but with great difficulty. As with Comm 1, the viscosity of the material was the major source of mechanical difficulty.

Obtaining samples of Comm 2 was relatively easy. However, after dispensing the 0.3 mL sample into the weighing pan, it was obvious that the solids content of duplicate samples was different.

The results of analyzing Comm 2 and Comm 3 are given in Table 9. As previously described, the method calls for running samples until duplicate results are within 1.5% of each other.

### 4.3.4 Evaluation of the Effect of the Response Factors

In Section 4.3.2.1, the accuracy of the THC values was concluded to be sufficient for capture efficiency determinations. This conclusion included evaluation of the closure data from the mixture runs. These values were based on an instrument response factor (RF) derived from averaging the individual responses for MEK and toluene. The language of Method 25A allows for deriving instrument RFs from other sources such as propane standards.

An investigation of the effects of such calibrations was conducted. The THC data from each of the mixture runs were recalculated on the basis of the MEK response and on the basis of the toluene response. The results of these calculations are given in Table 10.

The bias imparted to the results is relatively obvious in both cases. Basing the VOC concentrations of MEK leads to 122% closure while toluene

TABLE 9. VOLATILE CONTENT OF COATING MIXTURES

| Sample | Run No. | 1 | 2 | Average Volatile Content (%) | Coefficient of Variation[1] (%) | Meets Method Requirements (Y or N) |
|---|---|---|---|---|---|---|
| Comm 2 | 26 | 2.19 | 2.48 | 2.34 | 8.8 | N |
| Comm 2 | 23 | 2.43 | 2.41 | 2.42 | 0.6 | Y |
| Comm 2 | 23 | 2.57 | 2.64 | 2.61 | 1.9 | N |
| Comm 2 | 23 | 2.65 | 2.58 | 2.62 | 1.9 | N |
| Comm 3 | 31 | 19.8 | 13.3 | 16.6 | 27.8 | N |
| Comm 3 | 31 | 13.0 | 11.8 | 12.4 | 6.8 | N |
| Comm 3 | 31 | 14.4 | 14.5 | 14.5 | 0.5 | Y |

[1] Coefficient of variation = standard deviation as a percentage of the mean.

TABLE 10. COMPARISON OF RF FACTORS ON CLOSURES FOR MEK/TOLUENE MIXTURE EXPERIMENTS

| Run No. | Method 25A - THC | | | Method 18 - Speciated | | |
|---|---|---|---|---|---|---|
| | Closure from MEK RF (%) | Closure from Toluene RF (%) | Closure from Combined RF (%) | Closure from MEK (%) | Closure from Toluene (%) | Closure from Average (%) |
| 4 | 113 | 71.2 | 92.8 | 118 | 94.0 | 106 |
| 7 | 122 | 76.0 | 100 | 97.1 | 63.9 | 80.5 |
| 9 | 136 | 85.7 | 112 | 132 | 111 | 122 |
| 10 | 111 | 69.2 | 91.1 | 57.4 | 18.3 | 37.9 |
| 11 | 121 | 75.8 | 99.2 | 127 | 103 | 115 |
| 13 | 121 | 76.5 | 99.8 | 118 | 105 | 112 |
| 16 | 123 | 76.7 | 100 | 104 | 105 | 105 |
| 17 | 120 | 74.3 | 97.7 | 110 | 163 | 137 |
| 18 | 128 | 80.4 | 105 | 131 | 112 | 122 |
| Mean | 122 | 76.2 | 99.7 | 110.5 | 97.2 | 104 |
| CV (%) | 6.1 | 6.3 | 6.2 | 21.0 | 40.2 | 28.1 |

gives 76.2% closure. Each of these is far outside the allowable 10% variance.

By mathematically averaging the RFs before computing the concentrations, the more acceptable mean closure value of 99.7% is obtained. It is not clear from this limited data whether mathematical combining of RFs is appropriate for other ratios of solvent mixtures. The only clear conclusion is that calibration of the analyzer must be performed using the same solvents that will be later analyzed.

Calibration of the Method 18 analyzer was effected by determining individual RFs. Additionally, in calculating closures, each RF was applied to the appropriate peak to calculate its concentration. For completeness, the Method 18 data for the mixture experiments is shown in Table 10. All of the conclusions given in Section 4.3.2.1 remain valid for the individual compounds. In fact, the variability experienced with toluene separately is even higher than for any of the combined data.

## 4.4 QUALITY ASSURANCE AND QUALITY CONTROL

The assessment of overall performance of the VOC capture efficiency bench-scale testing was based upon performance and systems QA audits and upon internal QC data generated throughout the testing program. This section summarizes the results of the QA/QC program, which are reported in detail in a separate report titled "Measurement of Process Capture Efficiency Quality Assurance for Bench-Scale Testing".

Since the primary emphasis of the liquid/gas-phase mass balance tests was upon evaluation of Method 18 and Method 25A VOC measurements, this analysis emphasizes assessment of error (i.e., uncertainty) associated with Method 18 and Method 25A measurements. This assessment indicates that the measurement data collected during the bench-scale tests are sufficiently reliable to be used for evaluation of the feasibility of the liquid/gas-phase mass balance approach.

Multipoint performance audit data for the two VOC measurement methods (i.e., Method 18 and Method 25A) generally indicated that, at the time of the audit, there was no statistically significant, overall difference between the two methods, with respect to bias (i.e., systematic error). The multipoint audits indicated that, for both methods, bias for measurements of methyl ethyl ketone (MEK) and toluene concentrations was not significant. Observed bias for multipoint audit data using propane gas mixtures was, however, statistically significant for both Method 18 and Method 25A analyses, at -7.2% and -8.8%, respectively.

While the performance audit data indicate comparable results for both methods on the day these analyses were performed, control sample results indicate that, over the long-term (i.e., over the duration of bench-scale testing), there was a statistically significant difference in measurements made by the two methods. These data, based on daily analyses of a quality control gas mixture containing MEK and toluene, indicate that Method 18

results averaged about 5% lower than corresponding results for Method 25A analyses. This same trend is evident in the mass balance closure data for the evaporation tests using MEK and toluene. Differences between closure results for the two methods were also statistically significant, even when tested at the 99% confidence level. The average difference for closure data was approximately 12%.

In addition to providing a measure of relative bias between the two measurement methods, the control sample data also provide estimates of precision (i.e., measurement variability, or random error) for the two methods. For both methods, day-to-day variability (repeatability) was greater (i.e., the precision was poorer) than within-day variability (replicability). For both Method 18 and Method 25A, within-day variability was approximately 0.8%, expressed in terms of the coefficient of variation (CV), or relative standard deviation. Repeatability for Method 18 was not as good as that for Method 25A, with day-to-day CVs of 3.2% and 1.5%, respectively.

Control sample analyses represented an internal QC procedure designed to provide an estimate of sampling/analytical precision, as well as controlling this aspect of data quality within acceptable limits. In addition to control sample analyses, several other QC procedures were used to control measurement data quality. These included checks of and acceptance criteria for instrument response linearity, response factor variability, blank analyses, and instrument drift. Specified acceptance criteria were met in all but a few cases, and these QC checks generally fell within or near the specified limits.

# SECTION 5

# FIELD TESTING

The laboratory testing led to the conclusion that the liquid/gas-phase material balance methodology tested was sufficient to determine VOC capture efficiencies under controlled conditions. Recommendations included a plant or field test of the liquid/gas-phase material balance methodology under conditions which are more complex than the laboratory tests, yet simple enough to evaluate the methods in a stepwise manner.

Selection criteria for a field test site included the following:

- a single coating line within a relatively confined area,
- long steady state production runs absent of frequent long breaks or process changes,
- a coating formulation containing only a few solvent components,
- good measurement locations on all liquid and gas streams,
- an indirect fired drying oven, and
- a solvent recovery type control device.

A number of plants were reviewed and considered for testing, including the plants visited in the Phase I study (feasibility evaluation). One plant reviewed, Plant A, met the majority of the criteria. It was finally selected as the test site after a pre-test visit and evaluation at the plant.

## 5.1 TEST SITE DESCRIPTION

Plant A operates a single magnetic tape coating line. The manufacturing process involves the application of a magnetic iron oxide coating to a polyester film substrate. After application of the coating, the polyester film is sliced into tape and loaded onto tape cassettes. The tape coating process typically operates 24 hours per day, five days per week.

For the purposes of the current program, the tape coating operation can be categorized into the following process units: (1) solvent storage, (2) coating preparation, (3) coating application, (4) drying, and (5) solvent recovery. A flow diagram of the entire coating operation is shown in Figure 3, and the separate process units comprising the manufacturing operation are described in the following subsections.

### 5.1.1 Solvent Storage

The solvent storage process area supplies and receives the two solvents used in the coating operation, solvent A and B. The solvent storage area consists of the following equipment:

- a 10,000-gallon solvent storage tank (solvent A),
- a 10,000-gallon solvent storage tank (solvent B),
- a 10,000-gallon premix solvent storage tank,

- a 10,000-gallon distillate solvent storage tank, and
- associated distribution equipment (transfer pumps, meters, and transfer piping and ductwork).

These equipment items are shown in Figure 3 and described below.

The solvent storage tanks are used to receive periodic shipments of virgin solvents. These tanks are also used to receive purified solvent fractions from the solvent recovery area. Solvents from these two tanks are metered as necessary into the premix tank to formulate a 75/25 weight percent solution of solvent B/solvent A. The solvents are metered and pumped as needed to various parts of the plant. The distillate tank is used as a temporary holding tank for unseparated solvent mixtures from the solvent recovery area.

All four solvent storage tanks are vented to the solvent-laden air (SLA) system. In this manner, solvent vapors generated by diurnal temperature changes and tank volume displacements are routed to the solvent recovery unit, resulting in a higher total plant solvent recovery efficiency.

### 5.1.2 Coating Preparation

The coating preparation process area consists of the following equipment, as shown in Figure 3:

- a 600-gallon mixer,
- two 1000-gallon mix tanks (T101 and T102),
- one 600-gallon mix tank (T103),
- mills,
- two 800-gallon milled slurry tanks (T151 and T152),
- three 1000-gallon staging tanks (T201, T202, and T203), and
- associated distribution equipment (transfer pumps, meters, and transfer piping and ductwork.

The purpose of the coating preparation process unit is the formulation of a coating slurry of the required composition, density, viscosity, and throughput. The processing steps of the coating preparation phase are described below.

As shown in the figure, the coating preparation process begins with the mixture of resins, magnetic iron oxide powder, and other solids with a 75/25 weight percent solvent solution of solvent B/solvent A. These components are blended to achieve a final mixture containing 40 weight percent solids. The mixing operation is performed on a batch basis using the mixer and mixing tanks T101, T102, and T103.

Following the mixing operation, the 40 weight percent solids solution is milled. Final solvent adjustments are made in milled slurry tanks T151 and T152.

After the slurry has been milled and adjusted to the desired specifications, the coating slurry batch is pumped to staging tank T201. Tank T201 is a supply/holding vessel that discharges to tank T202, one of the

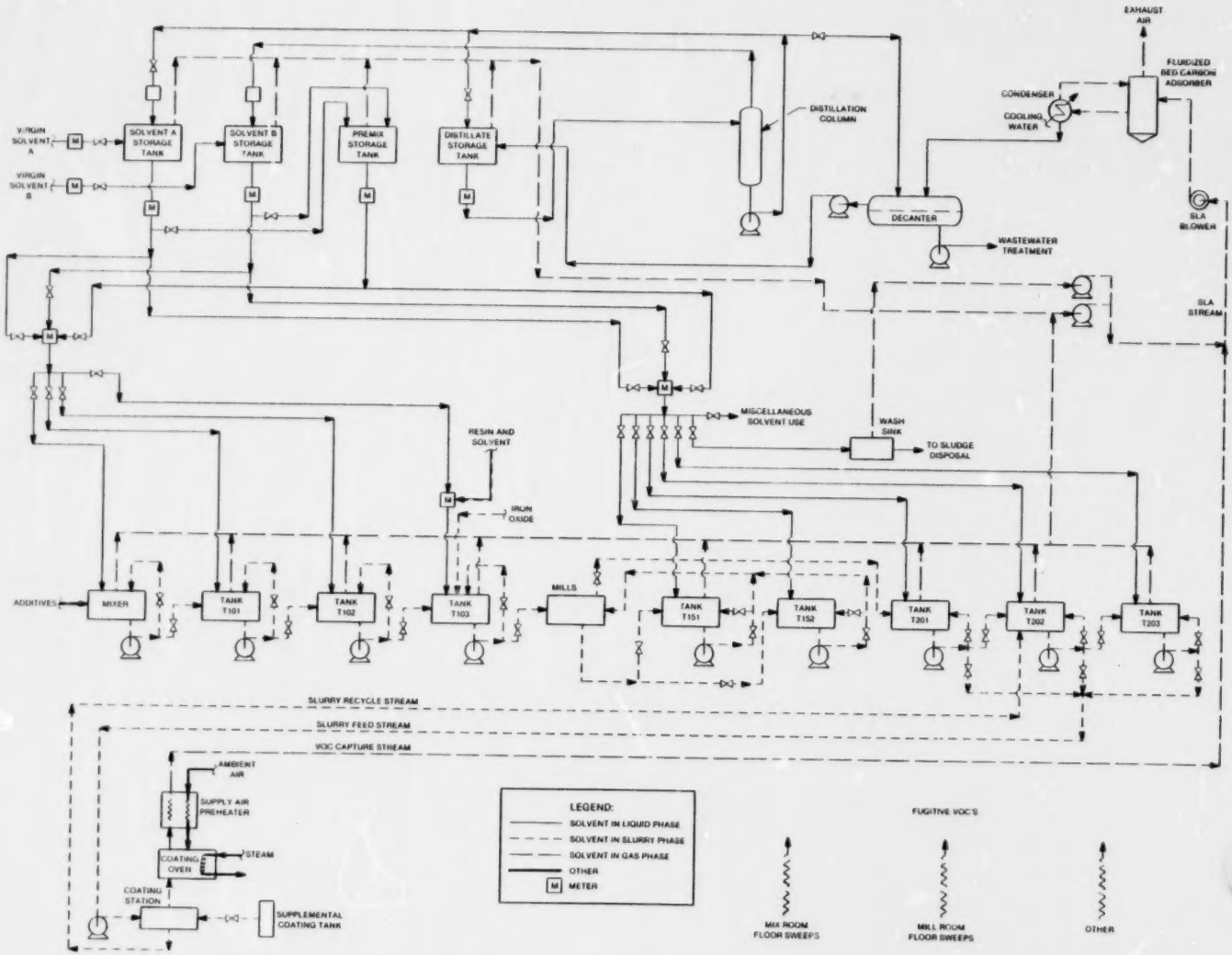


Figure 3. Detailed plant-wide flow diagram.

primary feed tanks for the coating station. The slurry is pumped in batch quantities from T201 to T202 between one and two times per each 24-hour period. Occasionally, solvent (solvent B) additions are made to the feed tank to adjust the viscosity, because of solvent losses during the holding/feed period. Tank T203 served as a spare feed tank during the test period.

As with the solvent storage process area, all tanks in the coating preparation process area are vented to the SLA system. Also, a covered wash sink located in the milling area is vented to the SLA system. The sink contains a solvent bath for intermittent manual cleaning of tools and parts.

Two floor sweep exhausts are located at the floor levels behind the tanks in each of the mixing and milling rooms. The floor sweeps are exhausted to the roof and discharged to the outside ambient atmosphere.

### 5.1.3 Coating Application

The coating application process unit consists of the following equipment:

- a single coating line,
- supplemental coating tanks, and
- associated distribution equipment (transfer pumps and transfer piping and ductwork).

These equipment items are shown in Figure 3 and are described below.

From primary feed tank T202 (in the milling room), the coating slurry is pumped to the coating station which is located in the adjacent coating room. The coating station is maintained within a small vented permanent enclosure extending to the entrance of the drying oven. The enclosure exhaust is vented to the overhead drying oven. Within the coating station, supplemental coating containing VOC is added to the slurry, and the slurry is applied to the synthetic web material. The web is coated continuously, except for a very brief period during the splicing of the web rolls. During this period, no slurry is applied, but instead is recycled through a loop back to the feed tank (T202). During normal operation, approximately 28 gallons of slurry are used per hour.

The coating room has one exhaust in the general room area (outside the coating station enclosure) leading to atmosphere; however, it was not operational during the test. Use of chemical smoke tubes indicated that the coating station enclosure did not capture all of the emissions from the applicator and that some escaped into the general room area. During the test period, the enclosure doors were left open because of concentration buildups. Plans were being made at that time to increase the capture and exhaust in the enclosure. Smoke tests also indicated that the milling room was negative in pressure relative to the coating room, causing some minor air flow into that area.

### 5.1.4 Drying

The drying process unit consists of the following equipment:

- a steam-heated drying oven,
- a supply air preheater, and
- ductwork for transport of the various air streams.

These equipment items are shown in Figure 3 and described below.

After coating, the wet web is dried, i.e., the solvent is evaporated, in a steam-heated drying oven. The drying medium is a mixture of preheated ambient air and air from the coating station enclosure. The solvent laden oven exhaust air, referred to as the capture stream, is cooled by the supply air preheater and a chilled water coil. It then joins the tank vent stream to form the main or total SLA stream.

### 5.1.5 SLA System and Solvent Recovery

The solvent recovery process unit consists of the following major equipment items:

- a fluidized carbon adsorber bed (CAB) and related equipment,
- a recovered liquid decanter,
- fractionating columns, and
- associated piping and ductwork.

These equipment items are shown in Figure 3 and described below.

The feed for the solvent recovery system is the main SLA stream which collects the gaseous emissions from the plant through the SLA system. This system is comprised of two sub-systems: (1) the vent system from the various tanks and wash sink previously described and (2) the capture system from the coater and drying oven. The vent stream and capture stream join to form the main SLA stream on the roof immediately after the chiller on the capture stream.

The solvent recovery system features a fluidized bed carbon adsorber sized to process a total SLA flow rate of 11,000 scfm. The system uses beaded activated carbon in a continuous adsorption/regeneration process to remove solvent from the SLA at efficiencies of nominally 95 percent and higher depending on carbon age and other factors. After adsorption of solvent, spent carbon is regenerated with high-temperature nitrogen. A water-cooled condenser is then used to separate the nitrogen from the desorbed solvent. The nitrogen is recycled; the condensed solvent phase is continuously dewatered in a decanter and sent to the distillate holding tank. On a batch basis, condensed solvent is sent through the distillation unit separating it into the fractional components. The individual components (solvent A and solvent B) are metered and returned to the individual solvent storage tanks for reuse in the coating process.

## 5.2 TESTING APPROACH

The technical approach to the field testing can be logically divided into three areas. These are:

- Measurement of capture efficiency of the coating line (coating and drying only), using a liquid/gas-phase material balance.
- Measurement of other streams and calculation of material balances, including the overall plant recovery efficiency.
- Analyses of errors in material balance measurements and calculations.

### 5.2.1 Capture Efficiency Measurement

As previously described, capture efficiency by the liquid/gas-phase approach is determined by comparing the VOC mass of the captured gas stream with the VOC mass of liquid used or evaporated.

Figure 4 provides a graphic summary of the liquid and gaseous VOC streams flowing into and out of the coating area at Plant A.

Determination of the gaseous VOC mass flow rate (GPMF) involves determination of the following:

- gas-phase VOC concentration in the capture stream,
- the volumetric flow rate of the capture stream, and
- the molecular weight of the VOC material.

At plant A, the captured VOC is directed into a single capture stream. Therefore, only a single measurement site is required.

Determination of the liquid VOC usage rate (LPMF) involves determination of the following:

- the coating slurry volumetric consumption rate,
- the slurry density, and
- the VOC weight fraction of the coating slurry.

At Plant A, it is not feasible to make the above determinations on a single coating slurry stream at the coater, because of the applicator configuration. Therefore, the determinations for each of the above must be made from the liquids at the slurry feed tank (102) and the supplemental coating tanks. The liquid mass flow rates are then added to yield the total liquid mass input.

### 5.2.2 Other Material Balances

Other stream measurements and material balance determinations seem advantageous during the field testing for verification of the coating room capture determinations and for determination of plant-wide emission reductions. They include:

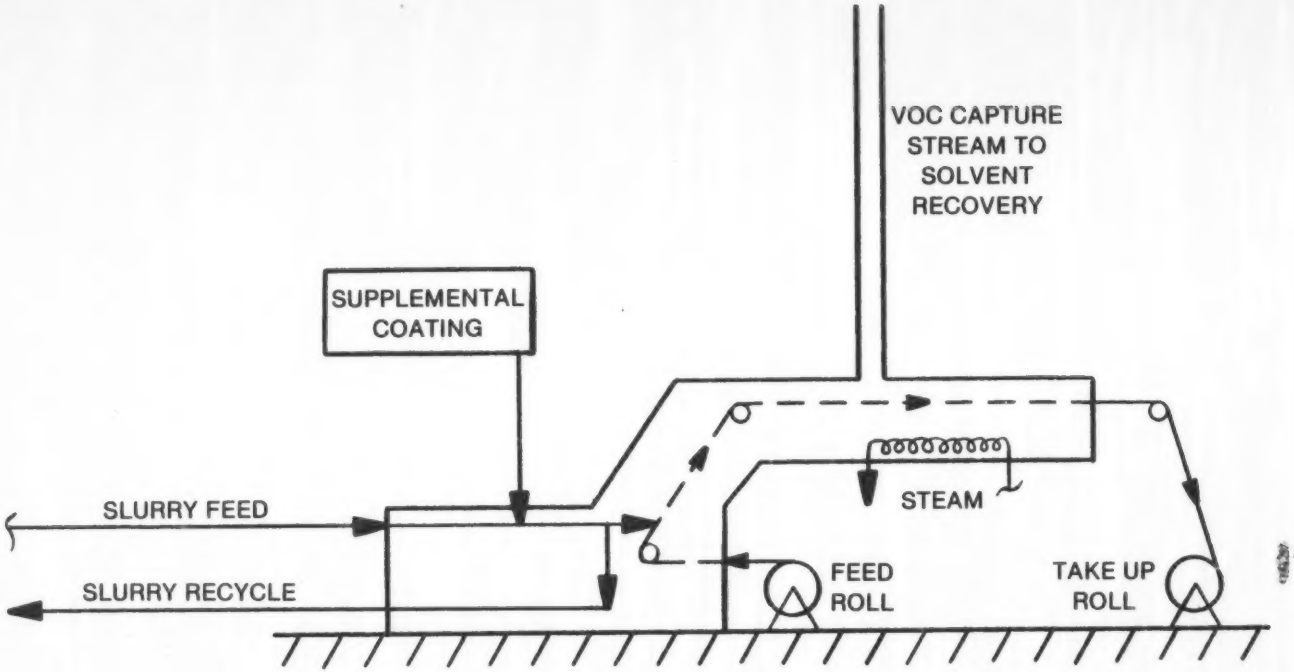


Figure 4. Coating area flow diagram.

- a gas-phase balance of SLA system streams,
- a liquid/gas-phase balance of recoverable VOC,
- the plant-wide capture efficiency, and
- the plant-wide recovery efficiency.

Figure 5 provides a simplified plant-wide flow diagram which may be useful in visualizing the following discussions.

5.2.2.1 Gas-Phase Balance of SLA Streams--

The purpose of this exercise is two-fold: (1) to provide a comparison between the sum of the measurements of the two individual SLA sub-system streams (capture + vent) and the main (total) SLA stream, and (2) to determine the fractional contribution of the two SLA subsystems to the total. Figure 5 shows the VOC mass flows of the two SLA subsystems into the main SLA stream. The VOC mass flow rate for each of the three streams is determined the same as that for the capture stream described in Section 5.2.1.

In the first case above, the sum of the measured vent and capture stream VOC mass flow rates should equal the measured VOC mass flow rate for the main SLA stream during the same period. This provides a relative verification of the VOC mass flow rate determinations for the two individual substreams. Referring to Figure 5, the comparison is made following Equation 3 below:

$$\text{Closure (\%)} = \frac{GPMF_{vent} + GPMF_{capture}}{GPMF_{main}} \times 100 \qquad (3)$$

where, GPMF = mass flow rate of VOC in the various gas streams, (lb/hr).

In the second case, a comparison of the two individual SLA subsystem mass flow rates to the sum of the two determines the fractional amount of VOC collected from each system. Therefore, a comparison can be made between the VOC collected from the coating operation and that collected from the other process units.

5.2.2.2 Liquid/Gas-Phase Balance of Recoverable VOC--

The purpose of this exercise is to verify the gas stream VOC mass flow measurements by comparison with liquid VOC mass flow measurements. The VOC mass entering the control device should equal the VOC mass exiting. Referring to Figure 5, Equation 4 below is used to calculate the liquid/gas closure:

$$LPMF_{\text{Recovered Solvent}} = GPMF_{\text{Vent}} + GPMF_{\text{Capture}} - GPMF_{\text{Outlet Stack}} \qquad (4)$$

where, LPMF = mass flow rate of liquid VOC in the form of recovered solvent (lbs/hr).
GPMF = mass flow rate of VOC in each gaseous stream (lbs/hr).

All gaseous VOC mass flow rates are determined as described for the captured VOC stream in Section 5.2.1.

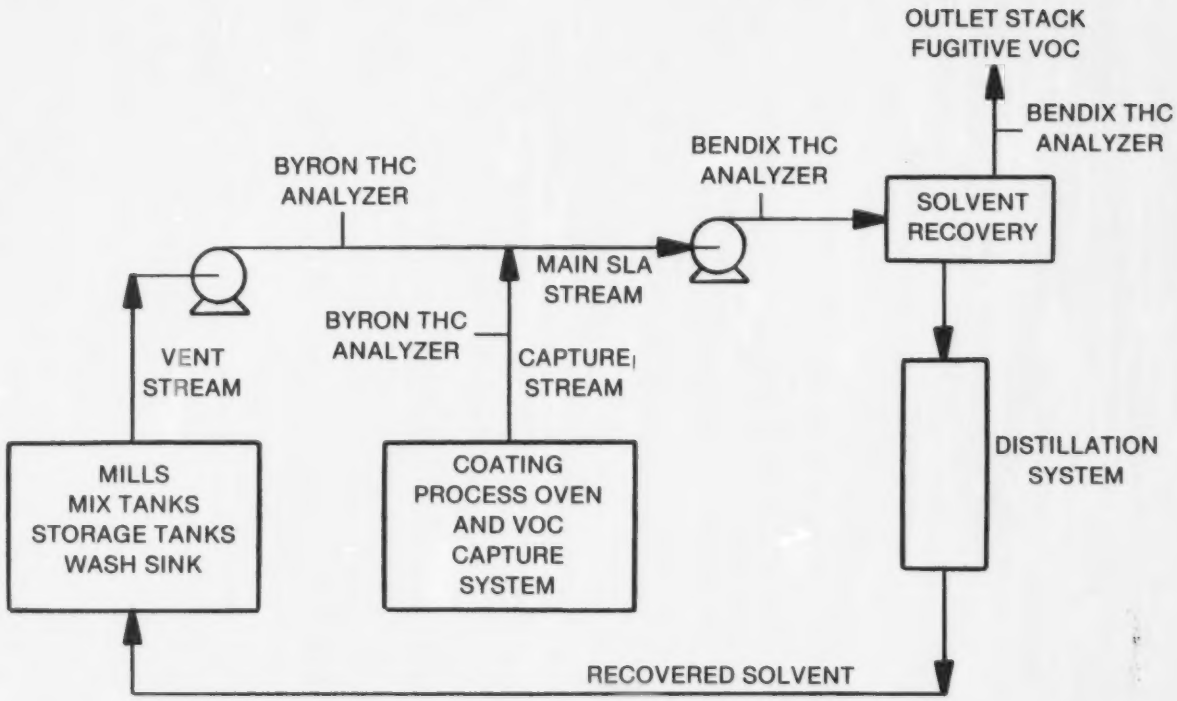


Figure 5. Simplified plant-wide VOC flow diagram.

Since the recovered liquid solvent stream is not metered and is not measurable at a single point on a continuous basis, the simplest determination is the combination of mass determinations for resultant streams. The total recovered VOC mass is equal to the sum of the metered pure solvent masses recovered and the net increase in the distillate tank VOC inventory from the start to the end of the period.

5.2.2.3 Plant-Wide Capture Efficiency--

The purpose of this exercise is to determine the percentage of the total VOC emissions from all VOC handling areas that are captured and delivered to the control device. This determination is similar to the liquid/gas capture efficiency determination for the coating area, described in Section 5.2.1, and requires measurement of the same parameters. However, it includes all of the process units in the tape coating plant and, therefore, requires a slightly different measurement approach. The plant-wide capture efficiency is calculated according to Equation 5 below:

$$CE_p = \frac{GPM_p}{LPM_p} \times 100 \qquad (5)$$

where, $CE_p$ = Plant-wide Capture Efficiency, (%).
$GPM_p$ = Mass of gaseous VOC collected by the SLA system from the entire plant during a test period, (lbs).
$LPM_p$ = Mass of liquid VOC vaporized throughout the tape plant during a test period, (lbs).

In the plant-wide capture efficiency determination, the liquid mass of VOC vaporized, i.e. VOC emissions, is not as easily determined as in the coating room area. This is complicated by the recycling of recovered solvent to the solvent storage and feed tanks, exhausting VOC mass from the feed tanks through the tank vent system, and the large fluctuations of liquid mass held in tanks within the plant. There are two methods for estimating the total VOC mass vaporized, however, both involve complex indirect determinations. The first solely involves liquid-phase measurements of the solvent flowing into the plant adjusted by net change in the inventory level within the plant during the test period. The second involves a determination of the total VOC emissions as the sum of captured and uncaptured emissions. The uncaptured emissions are determined indirectly by subtracting the mass exhausted from the control device from the total plant loss value (difference between starting and ending liquid inventories).

The gaseous VOC mass for the plant-wide capture efficiency determination is the total SLA stream or the sum of the VOC mass flows for the vent and capture streams.

5.2.2.4 Plant-Wide Recovery Efficiency--

The purpose of this exercise is to determine the percentage of the total vaporized VOC that is recovered. Conversely, the percentage of the total solvent used and lost to fugitive emissions can be determined.

The plant-wide recovery efficiency is determined by comparing the measured mass of recovered solvent with the total measured mass of VOC vaporized, as shown in Equation 6 below:

$$RE_p = \frac{LPM_{recov.}}{LPM_p} \times 100 \qquad (6)$$

where, $RE_p$ = Plant-wide recovery efficiency, (%).
$LPM_{recov.}$ = Mass of liquid VOC recovered during a test period, (lbs).
$LPM_p$ = Mass of liquid VOC vaporized during a test period, (lbs).

The mass of VOC vaporized is determined as described in Section 5.2.2.3. The total mass of recovered solvent is determined as described in Section 5.2.2.2.

5.2.3 Error Analysis

In order to determine the reliability of the material balance data obtained in this test, it is necessary to determine the precision and accuracy of the measurements and to conduct an error propagation analysis of the theoretical calculations.

The precision may be estimated based on observed variability in results from multiple determinations. The reliability of such an estimate increases with the number of measurements.

Once the precision of each parameter is estimated, statistical techniques can be used to estimate the overall uncertainty in the capture efficiency determination. Standard error propagation techniques involving Monte Carlo simulations yield estimates of confidence intervals and the minimum time necessary to adequately characterize the capture efficiency.

5.3 TEST METHODS AND PROCEDURES

This section describes the sampling and analytical methods and procedures used in measuring the individual parameters described in the previous section. The methods are summarized in Table 11.

5.3.1 Liquid-Phase Measurements

Liquid-phase measurements included liquid volume, density, and solvent content at set frequencies throughout the plant. These determinations were made on each accessible VOC containing liquid stream and tank throughout the tape coating plant.

5.3.1.1 Liquid Volume--
The liquid volume used during any time period was determined by the difference between inventory levels at the beginning and end of each period plus any volumetric adjustment transfer made on the tank. Liquid volumes were determined for the main coating slurry tank (102) at least hourly and at the beginning and end of tank refill period. All other streams and tanks were measured approximately every eight hours.

TABLE 11. SUMMARY OF SAMPLING/ANALYTICAL METHODS

| Measurement Parameter | Measurement Method(s) |
|---|---|
| Liquid-Phase Mass | Gravimetric Measurement of Density and Volumetric Measurements by Tank Depth or Meter Reading |
| Liquid-Phase Volatile Content | EPA Method 24 |
| Gas Velocity/Volumetric Flow Rate[a] | EPA Methods 1 and 2 using an S-type pitot |
| Gas-Phase VOC Concentration | (1) EPA Method 25A (Byron 401 and Bendix Continuous THC Analyzer) |
| | (2) Draft EPA Method 18 (speciation using GC/FID) |

[a]Temperature was measured using type K thermocouples; since the sample gas consisted primarily of air, a molecular weight of 29.0 was assumed for flow rate calculations.

Liquid inventory volumes in tanks were determined by making depth measurements and applying depth/volume conversion factors for each tank to the measurements. Depth measurements were performed using attached sight glasses and depth scales on tanks containing transparent liquids, and by hand held meter sticks on tanks containing coating slurry. Depth gauge readings were taken to the nearest 1/8 inch.

Volumetric transfers of pure solvents to and from tanks were determined by reading totalizer meters on the streams. Readings were to the nearest gallon.

5.3.1.2 Density--

Density of each liquid stream was determined at approximately eight-hour intervals. Individual 25 milliliter liquid samples were collected from each tank and weighed on a Mettler laboratory balance to the nearest 0.01 gram. The density was determined by calculating the mass to volume ratio.

5.3.1.3 Volatile Content--

The volatile or solvent content determinations were conducted at the same frequency as the liquid densities. The volatile content of liquid in each tank was determined by collecting liquid samples and conducting EPA Method 24 analyses. In this method, an accurately weighed slurry sample is mixed with a dispersing solvent and heated for 60 minutes at 110 $\pm$ 5°C. The weight lost during heating is assumed to be the volatile content of the slurry. For most analyses, a larger than specified sample size was used.

5.3.2 Gas-Phase Measurements

Gas-phase measurements in this test included volumetric flow rates and VOC concentrations in each of the major branches of the SLA system. These are described in the following paragraphs.

5.3.2.1 Gas-Phase Volumetric Flow Rates--

Flow rates were measured for the VOC capture stream, the tank vent stream, and the main SLA stream (CAB inlet). In general, each stream was measured three times per day using EPA Method 2.

Other miscellaneous measurements were made during the Method 2 traverses. Temperature of the gas was measured with a K-type thermocouple and calibrated digital read-out. Atmospheric pressure was obtained from the U.S. weather service. The relative humidity was measured during each traverse. The dry molecular weight of the gas stream was assumed to be 29.0 g/g-mole as described in Section 3.6 of Method 2.

Additionally, the gas flow rate in the SLA stream was monitored hourly using the plant in-line monitor. This provided observation for any major change in the flow during the test period.

5.3.2.2 Gas-Phase VOC Concentration--

Using a three-hole rake type probe, samples were collected from each SLA stream (vent, capture, main SLA and CAB outlet) and analyzed for VOC concentration. Analytical methods included EPA Method 25A and EPA Draft Method

18. The first method uses flame ionization detection (FID) to provide total hydrocarbon (THC) concentrations. Similarly, the second method also uses an FID for quantitation. However, organic species in the sample are chromatographically separated prior to detection.

The VOC concentration of each stream was measured continuously throughout the test period, except during calibration periods and one short period when the bottled air supply was depleted. Each measurement point is indicated on Figure 5.

EPA Method 25A--Method 25A specifies that THC determinations be performed using a continuous monitor equipped with an FID. This requirement was fulfilled in monitoring the carbon bed inlet (main SLA stream) and outlet (SLA exhaust) streams with Bendix Total Hydrocarbon Analyzers. The Bendix analyzers were supplied by the plant but calibrated according to the requirements specified in the QA project plan. Each of these analyzers was allowed to continuously analyze the appropriate stream during the entire test period.

Simultaneously, individual Byron model 401 analyzers were monitoring the THC content of the coating capture stream and the tank vent stream. In the THC mode, sample is introduced continuously into a sample loop. At sample injection, the loop contents are flushed into a restrictor column (empty 1/16 inch tubing) and eventually flow into the FID. A complete cycle is completed in one minute. At the completion of each analytical cycle, a built-in integrator provides the peak area data for recordation.

All data from the Byron instruments were automatically captured, stored on disk, and reduced using a microcomputer. Software to accomplish this was tailored for this project. In addition, the computer recorded date and time of analysis, instrument, analysis type, sampling location, and run number. As a backup to the microcomputer data acquisition system, integrated areas for each instrument were recorded on strip charts to provide hardcopy records of the analyses.

EPA Draft Method 18--Draft Method 18 differs from Method 25A in that sample acquisition may be performed either by direct interface or by grab sampling. In addition, the organic components of the stream are chromatographically separated prior to detection by FID.

The instrument and analytical conditions used were:

- Instrument — Shimadzu Model Mini-2
- Column — 6 ft. x 1/8 o.d. glass with SP2100 at 20% plus Carbowax 1500 at 0.1% on Supelcoport 100/120
- Carrier Gas — Nitrogen, approximately 40 mL/min
- Column Temperature — Isothermal, approximately 100°C
- Injection — 1 mL fixed volume loop
- Integrator — Hewlett Packard Model 3390A

Gas from the sample was flushed continuously through the sample loop. The injection valve was fitted with a Carle Model 4200 actuator controlled by an

adjustable Eagle Signal timer. The cycle time was set at 4 minutes for all analyses.

The integrated areas from the integrator hardcopy were input manually to the microcomputer data acquisition system. This step was very helpful in reporting results on a consistent basis. Additionally, it facilitated simple statistical analysis of the data using computer techniques.

## 5.4 RESULTS AND DISCUSSION

On-site testing consisted of 114 hours of analyses beginning at 0200 on 13 February 84 and ending at 2000 on 17 February 84. During this period, six discrete batches of slurry were prepared and applied to the web material. Detailed results of all analytical tests are presented in Appendix D. Sample calculations for determination of the liquid and gas masses are also given in Appendix D.

This section contains summaries of the results and discussions of those results. Testing results are presented in two categories: (1) coating area capture efficiency results and (2) other material balance results. Potential errors and their combined effects on the results and calculations are described in a third section.

The overall findings of the tests were as follows:

Coating Room Capture Efficiency (Method 25A) - 106.7%/103.0%
Coating Room Capture Efficiency (Method 18) - 105.1%
Gas-Phase Balance of SLA Streams (Method 25A) - 94.3%/92.9%
Gas-Phase Balance of SLA Streams (Method 18) - 99.4%/96.3%
Liquid/Gas Balance of Recoverable VOC - 81%
Measured Plant-Wide Capture Efficiency - 120%/94%
Measured Plant-Wide Recovery Efficiency - 86%/67%

### 5.4.1 Coating Area Capture Efficiency

As described in Section 5.2.1, the VOC capture efficiency in the coating area is determined as the ratio of gaseous VOC mass captured versus the liquid VOC mass used. A summary of the liquid/gas-phase mass flow rates and capture efficiencies from the tests is given in Table 12.

Initially, it was thought that the results obtained from the test data could be compared with an assumed capture efficiency value of 100 percent, since the coating room was totally enclosed and only vented to the capture stream. However, simple smoke tests during the test period indicated that this assumption was incorrect, and that in fact the potential existed for some minor uncaptured fugitive emissions. Therefore, the capture efficiency had to be considered somewhat less than 100 percent and the capture data evaluated by statistical methods.

The capture efficiencies presented in Table 12 demonstrate a substantial amount of variability on an hourly basis. This variability is more easily seen

TABLE 12. LIQUID AND GAS MASS FLOW RATES AND CAPTURE EFFICIENCIES FOR THE COATING ROOM

| Date | Time Interval | VOC Applied (Lb/Hr) | Capture Stream VOC Mass Flow Rate | | Capture Efficiency | |
|---|---|---|---|---|---|---|
| | | | Method 25A (Lb/Hr) | Method 18 (Lb/Hr) | Method 25A (%) | Method 18 (%) |
| 02/13 | 0200-0259 | 141 | 164 | 136 | 116 | 96.5 |
| | 0300-0359 | 118 | 146 | 134 | 123 | 113 |
| | 0400-0459 | 177 | 146 | NA | 82.5 | NA |
| | 0500-0559 | 88.8 | 146 | NA | 164 | NA |
| | 0600-0659 | 155 | 147 | NA | 94.8 | NA |
| | 0700-0759 | 133 | 144 | 138 | 108 | 103 |
| | 0800-0859 | 162 | 146 | 138 | 90.1 | 85.2 |
| | 0900-0959 | 69.4 | 145 | 137 | 208 | 197 |
| | 1000-1059 | 118 | 145 | 137 | 122 | 116 |
| | 1100-1159 | 139 | 143 | 136 | 102 | 97.8 |
| | 1200-1259 | 130 | 146 | 137 | 112 | 105 |
| | 1300-1359 | 95.6 | 146 | 137 | 152 | 143 |
| | 1400-1459 | 132 | 146 | 135 | 110 | 102 |
| | 1500-1559 | 160 | 145 | 134 | 90.6 | 83.8 |
| | 1600-1659 | 57 | 145 | NA | 254 | NA |
| | 1700-1759 | 133 | 126 | 114 | 94.7 | 85.7 |
| | 1800-1859 | 126 | 144 | 135 | 114 | 107 |
| | 1900-1959 | 142 | 143 | 135 | 100 | 95.1 |
| | 2000-2059 | 137 | 143 | 136 | 104 | 99.3 |
| | 2100-2159 | 119 | 119 | 123 | 100 | 103 |
| | 2200-2259 | 130 | 129 | 92.9 | 99.2 | 71.5 |
| | 2300-2359 | 139 | 143 | NA | 102 | NA |
| 02/14 | 0000-0059 | 160 | NA | NA | NA | NA |
| | 0100-0159 | 114 | NA | NA | NA | NA |
| | 0200-0259 | 114 | NA | NA | NA | NA |
| | 0300-0359 | 137 | NA | NA | NA | NA |
| | 0400-0459 | 137 | NA | NA | NA | NA |
| | 0500-0559 | 160 | NA | NA | NA | NA |
| | 0600-0659 | 160 | NA | NA | NA | NA |
| | 0700-0759 | 23.3 | 135 | NA | 579 | NA |
| | 0800-0859 | 134 | 137 | NA | 102 | NA |
| | 0900-0959 | 121 | 104 | NA | 86 | NA |
| | 1000-1059 | 110 | 138 | NA | 125 | NA |
| | 1100-1159 | 143 | 141 | NA | 98.6 | NA |
| | 1200-1259 | 111 | 147 | NA | 132 | NA |
| | 1300-1359 | 129 | 144 | NA | 111 | NA |
| | 1400-1459 | 136 | 145 | NA | 106 | NA |
| | 1500-1559 | 92.2 | 104 | NA | 112 | NA |
| | 1600-1659 | 137 | 150 | NA | 109 | NA |
| | 1700-1759 | 132 | 144 | NA | 109 | NA |

(continued)

TABLE 12 (continued)

| Date | Time Interval | VOC Applied (Lb/Hr) | Capture Stream VOC Mass Flow Rate | | Capture Efficiency | |
|---|---|---|---|---|---|---|
| | | | Method 25A (Lb/Hr) | Method 18 (Lb/Hr) | Method 25A (%) | Method 18 (%) |
| | 1800-1859 | 146 | 137 | NA | 93.8 | NA |
| | 1900-1959 | 123 | 134 | NA | 108 | NA |
| | 2000-2059 | 139 | 138 | NA | 99.3 | NA |
| | 2100-2159 | 140 | 134 | NA | 95.7 | NA |
| | 2200-2259 | 140 | 139 | NA | 99.3 | NA |
| | 2300-2359 | 98.3 | 113 | NA | 115 | NA |
| 02/15 | 0000-0059 | 151 | NA | NA | NA | NA |
| | 0100-0159 | 93.2 | NA | NA | NA | NA |
| | 0200-0259 | 163 | NA | NA | NA | NA |
| | 0300-0359 | 93.2 | NA | NA | NA | NA |
| | 0400-0459 | 94.2 | NA | NA | NA | NA |
| | 0500-0559 | 141 | 116 | NA | 82.3 | NA |
| | 0600-0659 | 118 | 132 | NA | 111 | NA |
| | 0700-0759 | 140 | 132 | NA | 94.3 | NA |
| | 0800-0859 | 104 | 85.8 | NA | 82.5 | NA |
| | 0900-0959 | 151 | 135 | NA | 89.4 | NA |
| | 1000-1059 | 81.1 | 109 | NA | 134 | NA |
| | 1100-1159 | 78 | 58.5 | NA | 75 | NA |
| | 1200-1259 | 132 | 68.7 | NA | 52 | NA |
| | 1300-1359 | 113 | 144 | NA | 127 | NA |
| | 1400-1459 | 107 | 95.6 | NA | 89.3 | NA |
| | 1500-1559 | 171 | 143 | NA | 83.6 | NA |
| | 1600-1659 | 114 | 121 | NA | 106 | NA |
| | 1700-1759 | 131 | 192 | NA | 146 | NA |
| | 1800-1859 | 147 | 155 | NA | 105 | NA |
| | 1900-1959 | 132 | 146 | NA | 110 | NA |
| | 2000-2059 | 148 | 146 | NA | 98.6 | NA |
| | 2100-2159 | 125 | 146 | NA | 116 | NA |
| | 2200-2259 | 117 | 146 | NA | 124 | NA |
| | 2300-2359 | 91.2 | 84.9 | NA | 93.1 | NA |
| 02/16 | 0000-0059 | 184 | NA | NA | NA | NA |
| | 0100-0159 | 93.2 | NA | NA | NA | NA |
| | 0200-0259 | 140 | NA | NA | NA | NA |
| | 0300-0359 | 140 | NA | NA | NA | NA |
| | 0400-0459 | 150 | NA | NA | NA | NA |
| | 0500-0559 | 100 | NA | NA | NA | NA |
| | 0600-0659 | 166 | 122 | NA | 73.5 | NA |
| | 0700-0759 | 87.1 | 122 | NA | 140 | NA |
| | 0800-0859 | 91.2 | 125 | NA | 137 | NA |

(continued)

TABLE 12 (continued)

| Date | Time Interval | VOC Applied (Lb/Hr) | Capture Stream VOC Mass Flow Rate | | Capture Efficiency | |
|---|---|---|---|---|---|---|
| | | | Method 25A (Lb/Hr) | Method 18 (Lb/Hr) | Method 25A (%) | Method 18 (%) |
| | 0900-0959 | 133 | 126 | NA | 94.7 | NA |
| | 1000-1059 | 147 | 126 | NA | 85.7 | NA |
| | 1100-1159 | 112 | 128 | NA | 114 | NA |
| | 1200-1259 | 135 | 137 | NA | 101 | NA |
| | 1300-1359 | 127 | 136 | NA | 107 | NA |
| | 1400-1459 | 76 | 62.9 | NA | 82.8 | NA |
| | 1500-1559 | 121 | 136 | NA | 112 | NA |
| | 1600-1659 | 143 | 135 | NA | 94.4 | NA |
| | 1700-1759 | 112 | 136 | NA | 121 | NA |
| | 1800-1859 | 146 | 136 | NA | 93.2 | NA |
| | 1900-1959 | 104 | 135 | NA | 129 | NA |
| | 2000-2059 | 99.3 | 133 | NA | 133 | NA |
| | 2100-2159 | 137 | 132 | NA | 96.4 | NA |
| | 2200-2259 | 139 | 135 | NA | 97.1 | NA |
| | 2300-2359 | 160 | 135 | NA | 84.4 | NA |
| 02/17 | 0000-0059 | 121 | NA | NA | NA | NA |
| | 0100-0159 | 137 | NA | NA | NA | NA |
| | 0200-0259 | 102 | NA | NA | NA | NA |
| | 0300-0359 | 126 | NA | NA | NA | NA |
| | 0400-0459 | 137 | NA | NA | NA | NA |
| | 0500-0559 | 137 | NA | NA | NA | NA |
| | 0600-0659 | 126 | NA | NA | NA | NA |
| | 0700-0759 | 131 | NA | 132 | NA | 100 |
| | 0800-0859 | 140 | 133 | 131 | 95 | 93.6 |
| | 0900-0959 | 147 | 138 | 130 | 93.9 | 88.4 |
| | 1000-1059 | 104 | 140 | 131 | 134 | 126 |
| | 1100-1159 | 183 | 137 | 128 | 74.9 | 69.9 |
| | 1200-1259 | 108 | 140 | 128 | 129 | 118 |
| | 1300-1359 | 111 | 136 | 126 | 122 | 113 |
| | 1400-1459 | 149 | 55.3 | 103 | 37.1 | 69.1 |
| | 1500-1559 | 141 | NA | NA | NA | NA |
| | 1600-1659 | 168 | 146 | NA | 86.9 | NA |
| | 1700-1759 | 96.3 | 97.4 | 129 | 101 | 134 |
| | 1800-1859 | 111 | 114 | 111 | 102 | 100 |
| | 1900-1959 | 83.1 | 108 | 111 | 130 | 133 |

NA - Not Analyzed

in the average capture efficiencies over an entire day as shown in Table 13. The coefficient of variation for individual method 25A data varies from 10.9 to 34.3% with an average of 23%. However, after being averaged or smoothed over a days time, the variation is reduced to 7.4%. For method 18 data, the reduction in variability is from 24.3% to 1.3%.

Another logical method of smoothing the data is to evaluate capture efficiencies during each discrete application batch. The results of such analyses are shown in Table 14. The amount of method 18 data was insufficient to include it in the table. For several batches, the start up and/or ending data were not included, because of non-steady state conditions.

These evaluations can be viewed as steady state determinations. The batch average capture efficiency of 103% appears to be somewhat better than the 106.7% when averaging by day. Additionally, the batch coefficient of variation of 4.6% is smaller than the 7.4% value from the daily average.

The fact that both mean values are greater than 100% is puzzling. The maximum capture efficiency possible is 100%, and the efficiency of this system is obviously expected to be somewhat less than that value. With the higher than expected values, one has to consider the entrance of an unmeasured source into the system or measurement bias as possible causes. A thorough review of the process revealed no unmeasured source of VOC. Based on the literature regarding the measurement methods used and on the detailed QA/QC program followed, there is no reason to believe that any of the measurement methods is biased high. Therefore, no reasonable explanation can be provided for the apparently high values.

Overall, the test data indicate that the liquid/gas conversion methodology can be used to determine reasonably reliable estimates of VOC capture efficiency around the coating room, as long as the limitations of this approach are taken into consideration. The limitations that exist include the need for long term averaging periods and fairly steady state operations. Only data collected during steady state conditions should be used in efficiency calculations. Also, the reliability of the estimate improves as the number of individual measurements increases.

The uncertainty in the capture efficiency determinations is analyzed in detail through an error analysis later in this section.

### 5.4.2 Other Material Balance Results

As described in Section 5.2.2, other material balances were included as part of the coating room capture efficiency test to verify measurements made in that test and to determine other efficiencies associated with the plant VOC control program. The results of these material balances are presented in the following paragraphs.

#### 5.4.2.1 Gas-Phase Balance of SLA Streams--

From the discussion in Section 5.2.2.1, it should be clear that the sum of the vent stream and capture stream VOC masses should equal the main SLA stream

TABLE 13. CAPTURE EFFICIENCY AVERAGES BY DAY

| Date | Average Capture Efficiency | | Coefficient of Variation (CV) for Hourly Data | |
|---|---|---|---|---|
| | Method 25A (%) | Method 18 (%) | Method 25A (%) | Method 18 (%) |
| 02/13 | 120.1 | 106.1 | 34.3 | 26.5 |
| 02/14 | 106.4 | ----- | 10.9 | ---- |
| 02/15 | 101.0 | ----- | 22.4 | ---- |
| 02/16 | 105.3 | ----- | 19.0 | ---- |
| 02/17 | 100.5 | 104.1 | 28.5 | 22.0 |
| Average | 106.7 | 105.1 | 23.0 | 24.3 |
| CV for 24 Hour Data | 7.4% | 1.3% | | |

TABLE 14. CAPTURE EFFICIENCY AVERAGES BY SLURRY BATCH

| Test Period | | | | Liquid-Phase Mass | Gas-Phase Mass Method 25A | Capture Efficiency Method 25A |
|---|---|---|---|---|---|---|
| Start | | Stop | | | | |
| (Date) | (Time) | (Date) | (Time) | (lbs) | (lbs) | (%) |
| 02/13 | 0200 | 02/13 | 0900 | 1037 | 1039 | 100.2 |
| 02/13 | 0900 | 02/14 | 0700 | 2860 | 3092 | 108.1 |
| 02/14 | 0800 | 02/15 | 0300 | 2430 | 2552 | 105.0 |
| 02/15 | 0400 | 02/16 | 0400 | 3071 | 2977 | 96.9 |
| 02/16 | 0500 | 02/16 | 2000 | 1751 | 1889 | 107.9 |
| 02/16 | 2100 | 02/17 | 1600 | 2543 | 2534 | 99.6 |
| Average | | | | | | 103.0% |
| CV for Batch Data | | | | | | 4.6% |

mass. A gas-phase mass balance is conducted by calculating the ratio of the sum of the two component stream masses to the main stream mass. The gas-phase mass flow rates and the associated material balances for the entire test period are presented in Table 15 on an hourly basis. Evaluations of the gas-phase closure results after smoothing are shown in Tables 16 and 17.

Table 16 shows the closure values and coefficients of variation when the hourly data are averaged over day long periods. The average closure by Method 25A was 94.3% and 99.4% by Method 18. The average coefficients of variation for the daily closures are 4.3% and 9.1%, respectively. This is considerably better than the 12.7% and 13.9% average coefficients of variation for the Method 25A and Method 18 hourly closure results.

Table 17 shows the closure values and coefficients of variation when hourly data are averaged over individual slurry batch use periods. The average closures by Method 25A and Method 18 were 92.9% and 96.3%, respectively, with average coefficients of variation at 2.5% and 8.8%.

In evaluating the discrepancy in the Method 25A closures, one potential source of error surfaced. It was determined from the Method 18 analyses that the vent stream contained a solvent B/solvent A ratio greater than the 75/25 ratio assumed for calculation purposes. The exact ratio could not be specified over the test period because only limited data were collected. An assessment of this factor indicates that the calculated VOC mass flow rates for the vent stream would be slightly lower than the actual values. The basis of this evaluation is presented in Section 5.4.3. However, the significance of this potential source of error is minimized since the vent stream mass flow rate is relatively small in comparison to the capture stream. Additionally, the same potential source of error likely affected the main SLA mass flow determinations to a lesser degree, thus tending to negate the net effect on the balance.

The closure values from both daily and batch data tend to confirm that the individual gas stream measurements are in agreement.

From the gas stream data for the entire test period, the fractional contributions for the vent system and the capture system to the total SLA load were determined to be approximately 20% and 80%, respectively.

5.4.2.2 Liquid/Gas Material Balance of Recoverable VOC--

From the discussion in Section 5.2.2.2, it can be seen that the liquid VOC mass recovered (recovered solvent) should equal the net recoverable VOC mass in the gaseous form (sum of gas-phase VOC mass input to the carbon bed minus the exhaust). The purpose of this comparison was to verify that the liquid and gas-phase mass measurements were equal.

The total recovered liquid VOC during the test was determined to be 13,450 pounds. When compared to 16,586 pounds, as determined by the gas-phase measurements over the same period, the net difference is approximately 21%.

The difference between the two calculated masses was greater than originally expected. However, it should be noted that the calculated gaseous

TABLE 15. GAS-PHASE MASS FLOW RATES AND MATERIAL BALANCES FOR THE SLA SYSTEM

| Date | Interval | Method 25A Mass Flowrates | | | Method 18 Mass Flowrates | | | Gas-Phase Closure | |
|---|---|---|---|---|---|---|---|---|---|
| | | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | EPA 25A (%) | EPA 18 (%)* |
| 02/13 | 0200-0259 | 164 | 32.4 | NA | 136 | NA | NA | NA | NA |
| | 0300-0359 | 146 | 27.7 | 181 | 134 | 29 | NA | 96 | 90.1 |
| | 0400-0459 | 146 | 28.6 | 183 | NA | 28.6 | NA | 95.4 | 95.4 |
| | 0500-0559 | 146 | 29.6 | 176 | NA | NA | 162 | 99.8 | 108 |
| | 0600-0659 | 147 | 29.7 | 186 | NA | NA | NA | 95 | NA |
| | 0700-0759 | 144 | 30 | 188 | 138 | NA | 171 | 92.6 | 98.2 |
| | 0800-0859 | 146 | 30.1 | 188 | 138 | NA | NA | 93.7 | 89.4 |
| | 0900-0959 | 145 | 31.7 | 188 | 137 | NA | NA | 94 | 89.7 |
| | 1000-1059 | 145 | 30.1 | 186 | 137 | NA | NA | 94.1 | 89.8 |
| | 1100-1159 | 143 | 29 | 186 | 136 | NA | NA | 92.5 | 88.7 |
| | 1200-1259 | 146 | 30 | 183 | 137 | NA | NA | 96.2 | 91.3 |
| | 1300-1359 | 146 | 29.6 | 183 | 137 | NA | NA | 96 | 91 |
| | 1400-1459 | 146 | 29.6 | 185 | 135 | NA | NA | 94.9 | 89 |
| | 1500-1559 | 145 | 29.3 | 182 | 134 | NA | NA | 95.8 | 89.7 |
| | 1600-1659 | 145 | 31.9 | 187 | NA | NA | NA | 94.6 | NA |
| | 1700-1759 | 126 | 29.3 | 160 | 114 | NA | NA | 97.1 | 89.6 |
| | 1800-1859 | 144 | 36.1 | 191 | 135 | NA | NA | 94.3 | 89.6 |
| | 1900-1959 | 143 | 33.3 | 191 | 135 | NA | NA | 92.3 | 88.1 |
| | 2000-2059 | 143 | 33.8 | 191 | 136 | NA | NA | 92.6 | 88.9 |
| | 2100-2159 | 119 | 33.1 | 135 | 123 | NA | NA | 112 | 115 |
| | 2200-2259 | 129 | 32.3 | 191 | 92.9 | NA | NA | 84.5 | 65.5 |
| | 2300-2359 | 143 | 30.8 | 191 | NA | NA | NA | 91 | NA |
| 02/14 | 0000-0059 | NA | NA | 191 | NA | NA | NA | NA | NA |
| | 0100-0159 | NA | NA | 188 | NA | NA | NA | NA | NA |
| | 0200-0259 | NA | NA | 186 | NA | NA | NA | NA | NA |
| | 0300-0359 | NA | NA | 188 | NA | NA | NA | NA | NA |
| | 0400-4059 | NA | NA | 194 | NA | NA | NA | NA | NA |
| | 0500-0559 | NA | NA | 209 | NA | NA | NA | NA | NA |
| | 0600-0659 | NA | NA | 194 | NA | NA | NA | NA | NA |
| | 0700-0759 | 135 | 41.3 | 197 | NA | NA | NA | 89.5 | NA |
| | 0800-0859 | 137 | 43.8 | 192 | NA | NA | NA | 94.2 | NA |
| | 0900-0959 | 104 | 40 | 162 | NA | 39.8 | NA | 88.9 | 88.8 |
| | 1000-1059 | 138 | 40.4 | 196 | NA | 42.8 | NA | 91 | 92.2 |
| | 1100-1159 | 141 | 34.8 | 180 | NA | 35.6 | NA | 97.7 | 98.1 |
| | 1200-1259 | 147 | 31.6 | 180 | NA | 31 | NA | 99.2 | 98.9 |
| | 1300-1359 | 144 | 30.6 | 183 | NA | 30.1 | NA | 95.4 | 95.1 |
| | 1400-1459 | 145 | 30.6 | 179 | NA | 29.9 | NA | 98.1 | 97.7 |
| | 1500-1559 | 104 | 19.8 | 122 | NA | 29.8 | NA | 101 | 109 |
| | 1600-1659 | 150 | 29.1 | 196 | NA | 30.3 | NA | 91.4 | 92 |
| | 1700-1759 | 144 | 29.3 | 176 | NA | 28.5 | NA | 98.5 | 98 |
| | 1800-1859 | 137 | 29.2 | 194 | NA | 29.3 | NA | 85.7 | 85.7 |
| | 1900-1959 | 134 | 28.3 | 189 | NA | 28.5 | NA | 85.9 | 86 |

(continued)

TABLE 15 (continued)

| Date | Interval | Method 25A Mass Flowrates | | | Method 18 Mass Flowrates | | | Gas-Phase Closure | |
|---|---|---|---|---|---|---|---|---|---|
| | | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | EPA 25A (%) | EPA 18 (%)* |
| | 2000-2059 | 138 | 28.4 | 189 | NA | 28.8 | NA | 88 | 88.3 |
| | 2100-2159 | 134 | 29.1 | 191 | NA | 30.4 | NA | 85.4 | 86.1 |
| | 2200-2259 | 139 | 31.2 | 194 | NA | 32.3 | NA | 87.7 | 88.3 |
| | 2300-2359 | 113 | 32.4 | 162 | NA | 34.4 | NA | 89.8 | 91 |
| 02/15 | 0000-0059 | NA | NA | 194 | NA | NA | NA | NA | NA |
| | 0100-0159 | NA | NA | 128 | NA | NA | NA | NA | NA |
| | 0200-0259 | NA | NA | 194 | NA | NA | NA | NA | NA |
| | 0300-3059 | NA | NA | 194 | NA | NA | NA | NA | NA |
| | 0400-0459 | NA | NA | 118 | NA | NA | NA | NA | NA |
| | 0500-0559 | 116 | 25.9 | 186 | NA | NA | NA | NA | NA |
| | 0600-0659 | 132 | 25.8 | 186 | NA | NA | NA | 76.3 | NA |
| | 0700-0759 | 132 | 33.1 | 194 | NA | NA | 161 | 84.8 | 98 |
| | 0800-0859 | 85.8 | 34.6 | 163 | NA | NA | 161 | 85.1 | 102 |
| | 0900-0959 | 135 | 38.7 | 176 | NA | NA | 94.9 | 73.9 | 126 |
| | 1000-1059 | 109 | 35.9 | 115 | NA | NA | NA | 98.7 | NA |
| | 1100-1159 | 58.5 | 30 | 139 | NA | NA | NA | 126 | NA |
| | 1200-1259 | 68.7 | 18.8 | 174 | NA | NA | NA | 63.7 | NA |
| | 1300-1359 | 144 | 35.6 | 172 | NA | NA | NA | 50.3 | NA |
| | 1400-1459 | 95.6 | 23 | 172 | NA | NA | NA | 104 | NA |
| | 1500-1559 | 143 | 34.9 | 166 | NA | NA | NA | 69 | NA |
| | 1600-1659 | 121 | 39.1 | 170 | NA | NA | 153 | 107 | 116 |
| | 1700-1759 | 192 | 51.7 | 170 | NA | NA | 148 | 94.2 | 108 |
| | 1800-1859 | 155 | 40.1 | 180 | NA | NA | 230 | 143 | 106 |
| | 1900-1959 | 146 | 39.2 | 180 | NA | NA | 176 | 108 | 110 |
| | 2000-2059 | 146 | 38.5 | 180 | NA | NA | 166 | 102 | 111 |
| | 2100-2159 | 146 | 38.6 | 180 | NA | NA | 163 | 102 | 113 |
| | 2200-2259 | 146 | 42.7 | 182 | NA | NA | 160 | 102 | 115 |
| | 2300-2359 | 84.9 | 44.7 | 131 | NA | NA | 167 | 103 | 113 |
| 02/16 | 0000-0059 | NA | NA | 184 | NA | NA | 114 | 98.9 | 113 |
| | 0100-0159 | NA | NA | 142 | NA | NA | 170 | NA | NA |
| | 0200-0259 | NA | NA | 184 | NA | NA | NA | NA | NA |
| | 0300-0359 | NA | NA | 182 | NA | NA | NA | NA | NA |
| | 0400-0459 | NA | NA | 184 | NA | NA | NA | NA | NA |
| | 0500-0559 | NA | NA | 187 | NA | NA | NA | NA | NA |
| | 0600-0659 | 122 | 33.6 | 187 | NA | NA | NA | NA | NA |
| | 0700-0759 | 122 | 34.7 | 191 | NA | NA | NA | 83.2 | NA |
| | 0800-0859 | 125 | 36.7 | 191 | NA | NA | NA | 82 | NA |
| | 0900-0959 | 126 | 37.5 | 189 | NA | NA | NA | 84.7 | NA |
| | 1000-1059 | 126 | 34.3 | 186 | NA | NA | NA | 86.5 | NA |
| | 1100-1159 | 128 | 31.8 | 184 | NA | NA | NA | 86.2 | NA |
| | 1200-1259 | 137 | 30.4 | 181 | NA | NA | NA | 86.8 | NA |
| | | | | | | | | 92.5 | NA |

(continued)

TABLE 15 (continued)

| Date | Interval | Method 25A Mass Flowrates | | | Method 18 Mass Flowrates | | | Gas-Phase Closure | |
|---|---|---|---|---|---|---|---|---|---|
| | | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | Capture (Lb/Hr) | Vent (Lb/Hr) | Main SLA (Lb/Hr) | EPA 25A (%) | EPA 18 (%)* |
| | 1300-1359 | 136 | 30.4 | 177 | NA | NA | NA | 94 | NA |
| | 1400-1459 | 62.9 | 31 | 87.4 | NA | NA | NA | 107 | NA |
| | 1500-1559 | 136 | 30.3 | 177 | NA | NA | NA | 94 | NA |
| | 1600-1659 | 135 | 31.2 | 180 | NA | NA | NA | 92.3 | NA |
| | 1700-1759 | 136 | 30.8 | 180 | NA | NA | NA | 92.7 | NA |
| | 1800-1859 | 136 | 31.8 | 187 | NA | NA | NA | 89.7 | NA |
| | 1900-1959 | 135 | 31.2 | 187 | NA | NA | NA | 88.9 | NA |
| | 2000-2059 | 133 | 33 | 192 | NA | NA | NA | 86.5 | NA |
| | 2100-2159 | 132 | 32 | 189 | NA | NA | NA | 86.8 | NA |
| | 2200-2259 | 135 | 31.8 | 187 | NA | NA | NA | 89.2 | NA |
| | 2300-2359 | 135 | 32.6 | 189 | NA | NA | NA | 88.7 | NA |
| 02/17 | 0000-0059 | NA | NA | 189 | NA | NA | NA | NA | NA |
| | 0100-0159 | NA | NA | 187 | NA | NA | NA | NA | NA |
| | 0200-0259 | NA | NA | 187 | NA | NA | NA | NA | NA |
| | 0300-0359 | NA | NA | 65.5 | NA | NA | NA | NA | NA |
| | 0400-0459 | NA | NA | 187 | NA | NA | NA | NA | NA |
| | 0500-0559 | NA | NA | 189 | NA | NA | NA | NA | NA |
| | 0600-0659 | NA | 32.5 | 189 | NA | NA | NA | NA | NA |
| | 0700-0759 | NA | 33.7 | 189 | 132 | NA | NA | NA | 87.7 |
| | 0800-0859 | 133 | 34.2 | 189 | 131 | NA | NA | 88.5 | 87.4 |
| | 0900-0959 | 138 | 34.8 | 182 | 130 | NA | NA | 94.9 | 90.5 |
| | 1000-1059 | 140 | 35.2 | 173 | 131 | NA | NA | 101 | 96.1 |
| | 1100-1159 | 137 | 32.8 | 175 | 128 | NA | NA | 97 | 91.9 |
| | 1200-1259 | 140 | 31.2 | 173 | 128 | NA | NA | 99 | 92 |
| | 1300-1359 | 136 | 30.8 | 173 | 126 | NA | NA | 96.4 | 90.6 |
| | 1400-1459 | 55.3 | 34.7 | 143 | 103 | NA | NA | 62.9 | 96.3 |
| | 1500-1559 | NA | NA | 176 | NA | NA | NA | NA | NA |
| | 1600-1659 | 146 | 40.3 | 164 | NA | NA | NA | 113 | NA |
| | 1700-1759 | 97.4 | 32.7 | 85.8 | 129 | NA | NA | 151 | 188 |
| | 1800-1859 | 114 | 32.7 | 35.7 | 111 | NA | NA | 410 | 402 |
| | 1900-1959 | 108 | 32.2 | 28.6 | 111 | NA | NA | 490 | 500 |

* Closure determined by combining the available Method 18 data with the other necessary Method 25A data.

TABLE 16. SLA GAS-PHASE MATERIAL BALANCES USING DAILY AVERAGING PERIODS

| Date | Average Gas-Phase Closure | | Coefficient of Variation (CV) for Hourly Data | |
|---|---|---|---|---|
| | Method 25A (%) | Method 18 (%) | Method 25A (%) | Method 18 (%) |
| 02/13 | 95.0 | 91.5 | 5.1 | 10.7 |
| 02/14 | 92.2 | 93.0 | 5.7 | 7.0 |
| 02/15 | 94.3 | 110.9 | 23.1 | 6.4 |
| 02/16 | 89.4 | ----- | 6.2 | ---- |
| 02/17 | 100.4 | 102.3 | 23.2 | 31.6 |
| Average | 94.3 | 99.4 | 12.7 | 13.9 |
| CV for Daily Data | 4.3% | 9.1% | | |

TABLE 17. SLA GAS-PHASE MATERIAL BALANCES USING SLURRY BATCH PERIODS

| Test Period | | | | Average Gas-Phase Closure | | Coefficient of Variation for Hourly Data | |
|---|---|---|---|---|---|---|---|
| Start | | Stop | | Method 25A | Method 18 | Method 25A | Method 18 |
| (Date) | (Time) | (Date) | (Time) | (%) | (%) | (%) | (%) |
| 02/13 | 0200 | 02/13 | 0900 | 95.4 | 96.2 | 2.6 | 7.8 |
| 02/13 | 0900 | 02/14 | 0700 | 94.8 | 89.7 | 5.9 | 11.3 |
| 02/14 | 0800 | 02/15 | 0300 | 92.4 | 93.0 | 5.8 | 7.0 |
| 02/15 | 0400 | 02/16 | 0400 | 94.3 | 110.9 | 23.1 | 6.4 |
| 02/16 | 0500 | 02/16 | 2000 | 90.0 | ----- | 7.0 | ---- |
| 02/16 | 2100 | 02/17 | 1600 | 90.4 | 91.6 | 12.0 | 3.6 |
| Average | | | | 92.9 | 96.3 | 9.4 | 7.2 |
| CV for Batch Data | | | | 2.5% | 8.8% | | |

mass value was based on measurements of two separate streams, and the recovered liquid mass was calculated from a combination of two separate meter readings and one tank measurement. The gas-phase measurements were discussed in the previous section.

Brief discussions are presented below regarding the reliability of the liquid measurements. Comparisons were made between the recovered solvent metered values and those determined by tank measurements.

The plant solvent A feed meter indicated that a total of 176 gallons or about 1271 pounds (solvent A density = 7.22 lb./gal.) was removed from the virgin tank during the test period. According to the depth gauge readings only 715 lb. were used. The difference of 556 pounds must be attributed to recovered solvent A. This value, when compared to the 91 gallons or 657 pounds registered by the dedicated solvent A recovery meter, indicates a discrepancy of approximately 15%.

Data for solvent B recovery corresponding to the analysis above show 669 gallons or 4951 pounds of solvent (solvent B density = 7.40 lb./gal.) removed through the main tank meter. Depth gauging indicates a gain of 3665 pounds during the test for a total of 8616 pounds. The recovered solvent B meter showed recovery of 1182 gallons or 8747 pounds. The difference of 1.5% is significantly less than that for solvent A.

5.4.2.3 Plant-Wide Capture Efficiency--

The concepts for determining plant-wide capture efficiency were discussed in Section 5.2.2.3. The approach followed in this determination was a comparison of VOC mass captured with VOC mass vaporized. Determination of the captured VOC was straightforward. However, determination of mass vaporized was extremely complex and indirect, because of the complicated recycling of recovered solvent and venting of the main storage tanks to the SLA system.

The total VOC captured and sent to the control device can be estimated by either the sum of the vent and capture streams or by the carbon adsorber inlet stream. Over the testing period, these values were 17,735 pounds and 18,825 pounds, respectively. For the remainder of this section, the captured mass is assumed to be that of the CAB inlet (18,825 pounds). The CAB inlet value was selected because it represents a single continuous measurement point and the other value involves combining measurements and potential sources of error.

An estimate of the total solvent evaporated during the test period can be obtained from the total amount flowing into the plant adjusted by the net change inside the plant. From the meter readings reported in Appendix D, 4900 pounds of solvent B, 1300 pounds of solvent A, and 5600 pounds of premix were fed into the plant during the test period. From Table 18, liquid inventory data, a net decrease of 3815 pounds is indicated for the inside inventory. The sum of the values is 15,619 pounds and represents a liquid measure of the solvent evaporated inside the plant. It should be noted that this value does not include the VOC vaporized in the outside tanks and distillation area which are captured by the vent system and sent to the recovery unit.

TABLE 18. LIQUID MASS INVENTORY DATA*

| Tank | 2/13 8:30 | 2/13 16:00 | 2/13 22:15 | 2/14 8:45 | 2/14 16:00 | 2/14 22:15 | 2/15 8:45 | 2/15 16:00 | 2/15 22:15 | 2/16 8:45 | 2/16 15:00 | 2/16 22:15 | 2/17 8:45 | 2/17 15:30 | 2/17 20:00 | Inventory Change (Start to Finish) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Mix Room** | | | | | | | | | | | | | | | | |
| T101 | 4430 | 4404 | 4397 | 1908 | 1863 | 1921 | 1942 | 1870 | 0 | 4773 | 4615 | 4602 | 4704 | 2637 | 2562 | -1868 |
| T102 | 4178 | 4164 | 4178 | 1856 | 6158 | 6144 | 6122 | 6122 | 5932 | 4113 | 4149 | 4149 | 4295 | 4164 | 4178 | 0 |
| T103 | 2475 | 2212 | 787 | 2385 | 2361 | 2344 | 2871 | 0 | 0 | 2568 | 2399 | 2370 | 754 | 0 | 0 | -2475 |
| Myers | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 3326 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| **Mill Room** | | | | | | | | | | | | | | | | |
| T151 | 4563 | 4563 | 4550 | 4507 | 1897 | 1371 | 0 | 1843 | 4149 | 4315 | 4315 | 4315 | 4471 | 4445 | 3083 | -1480 |
| T152 | 1846 | 300 | 1808 | 5239 | 5170 | 5176 | 4919 | 4926 | 4919 | 3567 | 1237 | 669 | 1476 | 4374 | 4473 | 2627 |
| T201 | 6125 | 5755 | 5689 | 2379 | 4908 | 5588 | 4743 | 4743 | 4773 | 3071 | 5365 | 4258 | 5037 | 5001 | 4062 | -2063 |
| T202 | 3523 | 5007 | 4214 | 5906 | 4921 | 4129 | 5211 | 4357 | 3587 | 5125 | 4356 | 5535 | 4054 | 3285 | 5004 | 1481 |
| Wash Sink | 574 | 581 | 552 | 559 | 552 | 552 | 574 | 581 | 581 | 596 | 581 | 588 | 596 | 581 | 537 | -37 |
| Inside Subtotal | | | | | | | | | | | | | | | | -3815 |
| **Bulk Storage** | | | | | | | | | | | | | | | | |
| Solvent A | 37916 | 35162 | 38393 | 38155 | 38393 | 38093 | 37916 | 38393 | 38039 | 36839 | 37078 | 37078 | 37078 | 37439 | 37201 | -715 |
| Solvent B | 41167 | 42041 | 41789 | 42285 | 42640 | 43122 | 43492 | 45313 | 42404 | 42404 | 43729 | 43729 | 43729 | 44951 | 44832 | 3665 |
| Premix | 27409 | 27284 | 27284 | 27048 | 22798 | 22445 | 22209 | 22445 | 22209 | 22092 | 22209 | 21974 | 21621 | 21739 | 21739 | -5670 |
| Distillate | 43066 | 43794 | 43794 | 43911 | 45132 | 44890 | 45728 | 45868 | 45368 | 45250 | 45853 | 45368 | 46802 | 47044 | 47280 | 4214 |
| Outside Subtotal | | | | | | | | | | | | | | | | 1494 |
| Total Inventory | 177272 | 175267 | 177435 | 176138 | 176793 | 175721 | 175727 | 176461 | 175281 | 174713 | 175886 | 174635 | 174617 | 175660 | 174951 | -2321 |

*All values are in pounds.

The total mass of VOC vaporized can also be viewed as the total mass of vapors formed. This mass can then be determined by summing the captured and uncaptured VOC masses. The captured mass is directly determined, while the uncaptured mass can only be indirectly determined. The uncaptured mass is equal to the 2321 pounds of total VOC lost from the plant (difference between beginning and ending liquid inventories) minus 1149 pounds of VOC mass exhausted from the control device. The mass of VOC captured and sent to control device was 18,825 pounds. The uncaptured VOC mass was 1172 pounds (2321 pounds - 1149 pounds). The total mass of vaporized VOC was therefore 19,997 pounds.

The overall capture efficiency determination using the first concept for approximating the mass of vaporized VOC is 120%. This compares to approximately 94% as determined using the second concept. Obviously, there cannot be more VOC captured than vaporized, thus demonstrating a significant amount of error in the first calculation. An obvious source of error is the exclusion of the tank and distillation vapors from the total emissions, and their inclusion in the total captured mass. Although the second calculation yields a value in the expected range, it is based on data which were obtained as indirectly as that for the first calculation, and must therefore be considered as equally prone to error.

5.4.2.4 Plant-Wide Recovery Efficiency--

The plant-wide recovery efficiency is the percentage of the total VOC mass vaporized which is recovered from the solvent recovery unit. The liquid recovered (13,450 pounds) can be compared with the VOC mass evaporated (15,619 pounds) or the mass of VOC vapors formed (19,997 pounds), as discussed in the previous section. The recovery efficiency values calculated by both methods are 86% and 67%. As in the previous section, these values were obtained using indirect methods and may be somewhat error prone.

In evaluating plant-wide recovery determinations, an attempt was made to close a complete material balance around the plant. From the VOC mass evaporated and recovery data, it can be seen that only 2169 pounds of the 15,619 pounds are unaccounted for. The most obvious source of fugitive losses is the carbon adsorber. Measurements of the carbon adsorber exhaust indicate that 1149 pounds of VOC were lost during the period. Measurements and calculations of VOC mass lost with the water discharge from the solvent recovery unit estimate a maximum loss of 2 pounds during the test period. The only obvious paths of VOC loss within the plant were floor sweep exhausts in the mixing and milling areas and product retention. Measurements of VOC concentrations and determinations of floor sweep flow rates yielded an approximation of fugitive losses totalling 192 pounds. No value was determined for the product retention. Totalling all sources accounts for 14,793 pounds or 95% of the solvent throughput.

5.4.3 Error Analysis

Monte Carlo simulations were used to derive estimates of overall uncertainty in the liquid/gas capture efficiency results for the coating room. Using the Monte Carlo simulation technique, 400 closure estimates were

generated from a "typical" set of measurement data. With this technique, each measurement parameter (e.g., gas flow rate for the capture stream, VOC concentration of the capture stream, liquid density, etc.) was perturbed randomly to simulate the actual variation that would occur in repeated measurements under a single set of process conditions. A Guassian distribution was assumed in simulating this variation.

Error estimates used in the simulation included both random and systematic error components corresponding to error resulting from imprecision (i.e., random variability in replicate measurements) and to error resulting from measurement bias. For instance, replicate measurements of liquid density were found to have a precision of 1.3%, expressed in terms of the coefficient of variation. Performance audits of the density measurements indicated an average bias of -0.04% with a standard error of 1.3%. For the coating line liquid/gas closure simulation, a "typical" liquid density of 1.25 g/ml was used. This input value was varied in each of 400 closure calculations, according to the input error estimates. In other words, the error statistics were used to generate the simulated density measurement values which were in turn used to calculate liquid/gas closure. The resulting set of closure results is thus a simulation of results which would theoretically be obtained if 400 closure measurements could be made under a single set of process conditions. The statistical distribution of this simulated data set were then used to derive estimates of uncertainty for the actual closure data as discussed below. Input values and error estimates for measurement parameters used in the Monte Carlo simulation of coating line liquid/gas closure are shown in Table 19.

The output of the Monte Carlo simulation is a set of closure values, which is assumed to be statistically representative of the population of all possible measurements which could be made under the given set of process conditions. Assuming that a similar relative distribution would be expected under any other set of process conditions, these results may be used to estimate relative uncertainty in the actual closure estimates. For the coating line liquid/gas closure, the Monte Carlo simulation indicated a relative bias of -3.9% in measured closure. In other words, if repeated measurements were made of a process where the actual closure was 100%, the mean measured value would approach 96.1%. The simulation further indicated that approximately 95% of the individual measurements in such a case would be between 80% and 120%, since more than 95% of the 400 simulated values fell within $\pm$20% of the "true" value. Approximately 74% fell within $\pm$10% of the true value and slightly more than 38% fell within $\pm$5%.

The error distribution described above may be used to define the probable uncertainty associated with any single closure measurement. For a single measurement for example, there is a probability of 38% that it is within $\pm$5% of the true value, and a 95% probability that it is within $\pm$20% of the true value. In practice, however, closure estimates would rarely be based on a single determination. Rather, repeated measurements would likely be made and the average of these reported as the closure estimate. Error in such an estimate is substantially reduced since some of the random measurement variability tends to be averaged out. Overall error in the closure estimate becomes smaller as the number of individual measurements used to compute the estimates becomes

TABLE 19. INPUT VALUES FOR MONTE CARLO SIMULATION OF COATING LINE LIQUID/GAS CLOSURE MEASUREMENTS

| Measurement Parameter | Input Value[a] | Coefficient of Variation[b] | Relative Bias[c] | |
|---|---|---|---|---|
| | | | Mean | Standard Error |
| Capture Stream VOC Concentration | 3150 ppm | 4% | -3.1% | 4.2% |
| Capture Stream Flow Rate | 3850 $ft^3$/min. | 4% | 0% | 3.1% |
| Capture Stream Molecular Weight | 77 g/g-mole | 0% | 0% | 0% |
| Liquid Density | 1.25 g/ml | 1.3% | -0.04% | 1.3% |
| Coating Mixture Volatile Fraction | 0.60 | 0.3% | 0.8% | 0.7% |
| Slurry Tank Hourly Volume Change from T to $T_2$ | 18 gal | 0% | 0% | 5% |

[a] Selected as representing a typical measured value.

[b] Standard deviation for replicate measuremnts, expressed as a percentage of the input value.

[c] Systematic error expressed as a percentage of the input value.

larger. Based on the Monte Carlo results for coating line liquid/gas closure, the mean of three measurements would, at the 95% confidence level, be expected to be within ±10.7% of the true value, while the mean of six measurements would be expected to be within ±7.6%. A plot of this relationship for different numbers of measurements is shown in Figure 6. These estimates are based on the relationship:

$$\sigma_{\bar{x}} = \sigma / \sqrt{n}$$

where,

$\sigma_{\bar{x}}$ = standard deviation of means,
$\sigma$ = standard deviation of the population from which the samples are drawn, and
n = number of samples used to compute the mean.

A Gaussian distribution is assumed in the above expression.

## 5.5 QUALITY ASSURANCE AND QUALITY CONTROL

This data quality assessment was based upon performance and systems QA audits and upon internal QC data generated throughout the field testing program. This section summarizes the results of the QA/QC program. Detailed QA/QC data and discussions are provided in a separate document titled "Measurement of Process Capture Efficiency, Quality Assurance Report for Field Testing".

The primary emphasis of this section is upon the gas phase VOC measurements using Methods 18 and 25A, although other measurements necessary for determining capture efficiency (e.g., density, volatile fraction, etc.) are also addressed. Overall, the QA/QC data indicate that the measurement data collected during the plant tests are sufficiently reliable to be used for evaluation of the feasibility of the liquid/gas-phase mass balance approach.

### 5.5.1 Method 25A

Performance audit data indicated that Method 25 VOC measurements were within the ±5% objectives for bias for all four instruments/sampling locations. Although the solvent B/solvent A ratio in the calibration gas mixture was different than that for the sample gas at some locations, there seemed to be no appreciable error in the results. This item is further discussed in Section 5.5.4. Control sample data for the Method 25A analyses indicated within-day precision ranging from 0.9% to 2.7%, expressed in terms of the pooled coefficient of variation. Between-day variability ranged from 1.2% to 4.0% for the four instruments.

### 5.5.2 Method 18

Method 18 performance audit results indicated that these analyses met the ±10% bias objectives specified in the QA Project Plan. Control sample data indicated within-day precision of 1.1% for solvent B and 0.7% for solvent A. Day-to-day variability of the control sample results was 4.8% and 4.0% for solvent B and A, respectively.

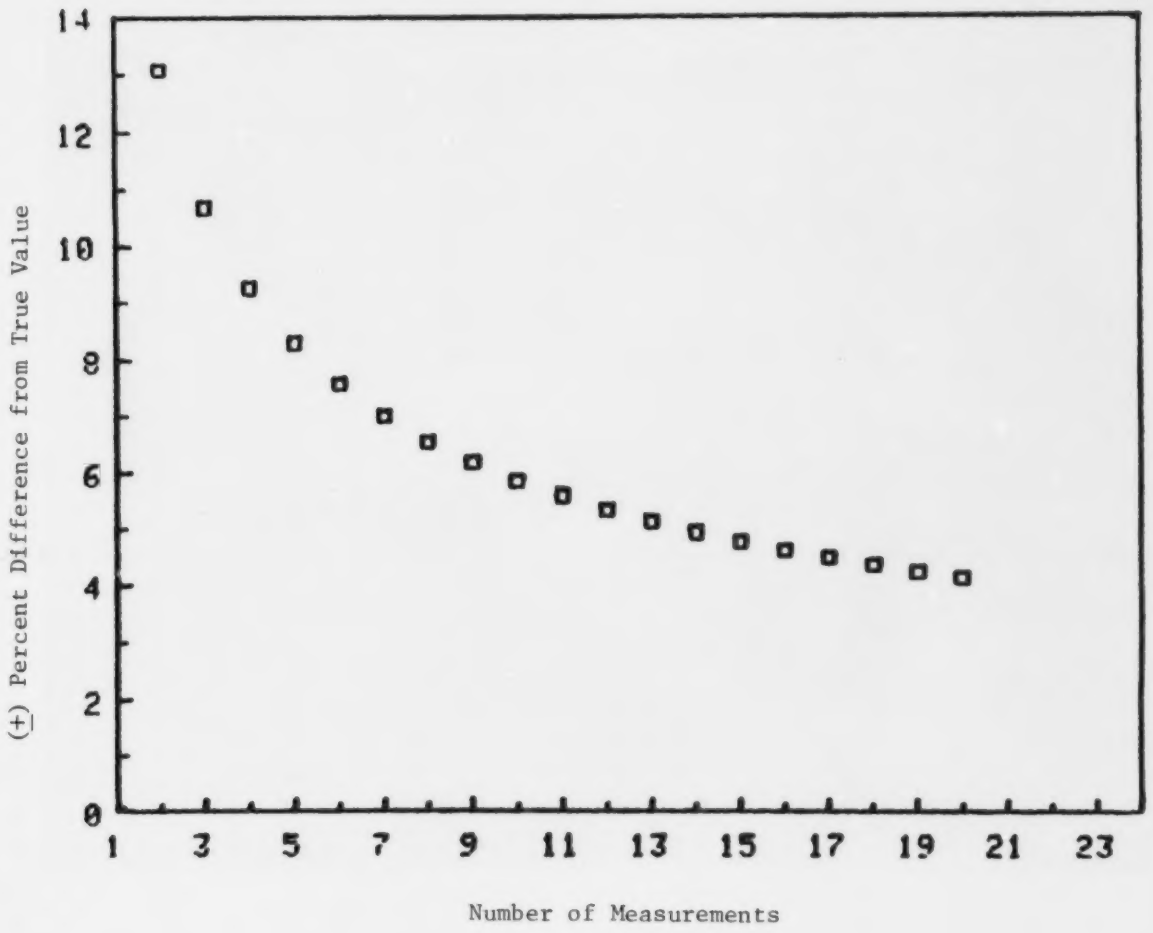


Figure 6. Range of error for means of multiple measurements of coating line liquid/gas closure.

### 5.5.3 Other Measurements

Performance audits of the density and volatile fraction determinations indicated that the relative error of both of these analyses was within ±2%. Audits of the balances indicated a maximum error of 0.04 g for a 100 g load.

### 5.5.4 Byron 401 Response Factors

All of the individual THC data given in Appendix D and summarized in Section 5 of this report were based on the response factors obtained from multipoint calibrations using certified mixtures of solvent A and solvent B.

Since flame ionization detectors used in VOC analyzers have differing detection efficiencies for different compounds, the response factor for the mixture changes with the ratio of the components. Therefore, if the instrument response factor is based on responses using a calibration stream with a different ratio than that in the measurement stream some error may exist in values determined.

In the field test, several streams such as the vent stream and carbon bed outlet are known to have component ratios different from those in the calibration. In particular, the CAB stack outlet is almost pure solvent B. This creates a question of what the impact might be on VOC data collected from streams with ratios different than that during calibration and on the resultant mass flow calculations.

To assess the potential impact, a series of known mixtures of solvent A and B were analyzed on a Byron 401 and the response factors calculated. The results of these are given in Table 20 and are shown graphically in Figure 7. These data yields a correlation coefficient of 0.9917. The slope of the linear least squares line is 0.002524 RF units per % solvent B. This model predicts an RF factor of 0.8760 for pure solvent A and 0.6237 for pure solvent B.

The plot of the experimental data for solvents encountered in this test yields a relatively shallow slope. This indicates that the difference in response factors for any combination of the two solvents should not be large, unless the difference between the expected ratio and actual ratio is large. For example, if the expected ratio of the measurement stream and the ratio used in calibration is 75/25 and the actual ratio is 80/20, the respective response factors should be 0.6867 and 0.6741. The difference in the response factors is less than 2 percent. In addition to the response factor, the carbon number and molecular weight for the mixture also change with the ratio of the components and play integral roles in the calculation of the mass flow rate. For the case above, inclusion of the carbon number and molecular weight for the calibration mixture also cause the calculated mass flow rate to be lower than the true value. For typical VOC mass flow rates in the capture stream (e.g. 130 lb./hr.) and the difference between the calibration and the actual ratio described above, the calculated value would be about 3.5 percent lower than the actual mass flow rate.

TABLE 20. BYRON 401 RESPONSE FACTOR VARIATIONS WITH COMPOSITION

| Run No. | Solvent B (ppmc) | Solvent A (ppmc) | THC (ppmc) | Solvent B[1] (%) | Solvent A[1] (%) | RF |
|---|---|---|---|---|---|---|
| 1 | 0 | 3448 | 3448 | 0 | 100 | 0.8990 |
| 2 | 4160 | 0 | 4160 | 100 | 0 | 0.6367 |
| 3 | 1335 | 2341 | 3676 | 36.3 | 63.7 | 0.7888 |
| 4 | 441 | 3082 | 3523 | 12.5 | 87.5 | 0.8373 |
| 5 | 208 | 3275 | 3483 | 6.0 | 94.0 | 0.8469 |
| 6 | 998 | 2620 | 3618 | 27.6 | 72.4 | 0.8014 |
| 7 | 1726 | 2017 | 3743 | 46.1 | 53.9 | 0.7614 |
| 8 | 2721 | 1193 | 3913 | 69.5 | 30.5 | 0.6899 |
| 9 | 3370 | 655 | 4025 | 83.7 | 16.3 | 0.6584 |
| 10 | 703 | 2865 | 3568 | 19.7 | 80.3 | 0.8268 |
| 11 | 2184 | 1638 | 3822 | 57.1 | 42.9 | 0.7327 |

(1) % by volume of the total VOC.

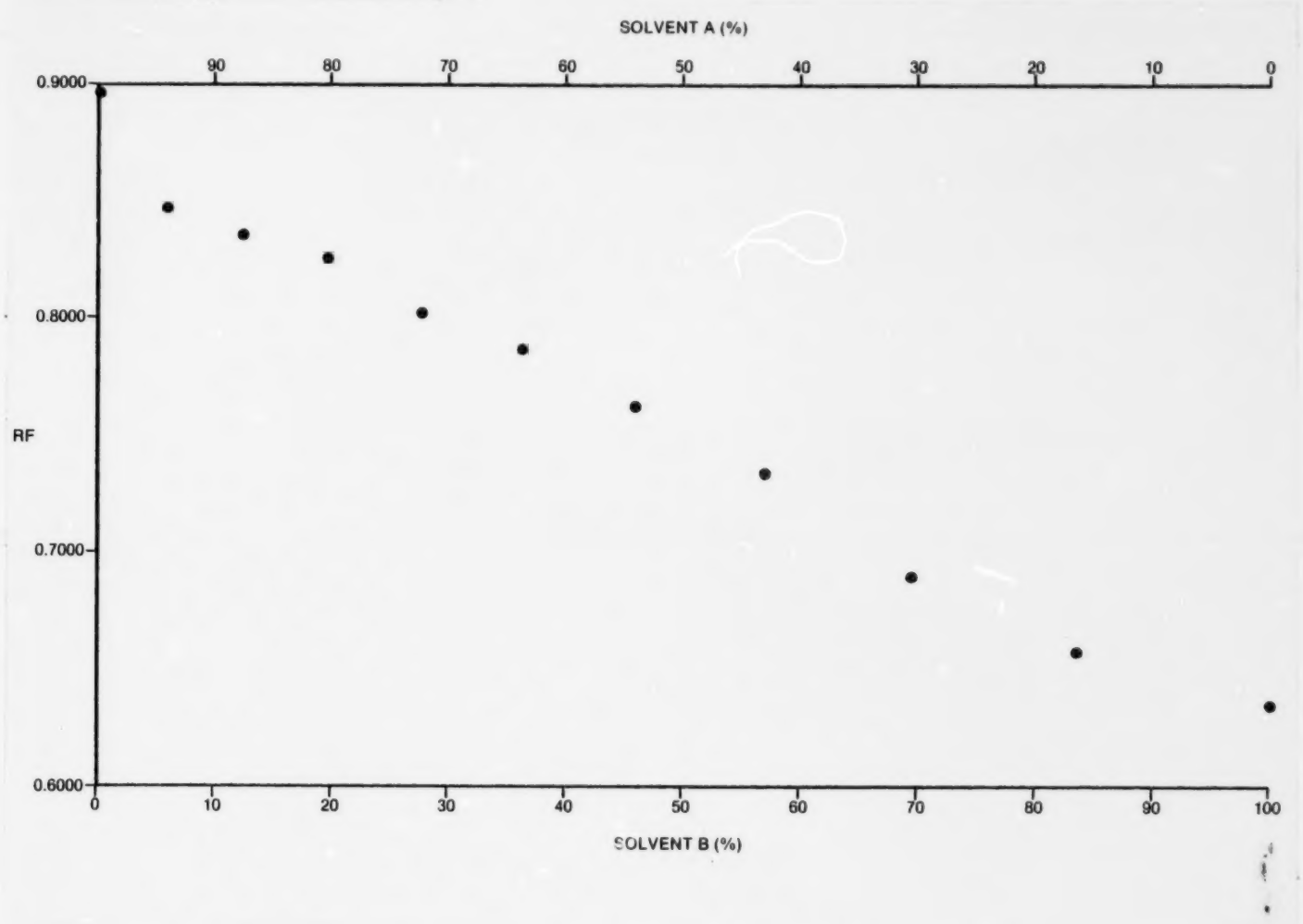


Figure 7. Response factor variations with compositions for a Byron 401.

For other solvent mixtures at other test sites, the degree of potential error due to assuming the wrong mixture ratio may be greater or less than that for the two solvents in this test. The magnitude of the potential error will be dependent on the degree of difference between the response efficiencies, carbon numbers, and molecular weights for the various organic components.

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## APPENDICES


APPENDIX A. Information Sources Reviewed . . . . . 98

APPENDIX B. Previous Liquid/Gas-Phase Tests Reviewed . . . . . 102

APPENDIX C. Laboratory Test Data and Calculations . . . . . *

APPENDIX D. Field Test Data and Calculations . . . . . *


*Appendices C and D may be obtained by writing to the U.S. EPA, Hazardous Waste Engineering Research Laboratory, 26 West St. Clair St., Cincinnati, OH 45268

# APPENDIX A

## INFORMATION SOURCES REVIEWED

## APPENDIX A

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# APPENDIX B

## PREVIOUS LIQUID/GAS-PHASE TESTS REVIEWED

Data from previous liquid/gas-phase testing are summarized in this appendix. Using the liquid/gas material balance technique, the amount of liquid solvent used at the coater is compared to the measured amount of VOC in the capture stream and the measured solvent removal of the control device. The liquid/gas-phase testing approach incorporates test methods used in both the liquid- and the gas-phase approaches. As discussed below, comparisons of liquid- and gas-phase measurements to complete a solvent mass balance around the system have met with varied degrees of success.

### B.1 PLANT 7

Plant 7 is a publication rotogravure facility using toluene as the solvent in the printing process. Two of the processes are equipped with unique VOC capture systems consisting of cabin-type structures enclosing the upper third of the presses. Air is drawn from the pressroom and up through the enclosures. Solvent vapors are captured by the induced air flow and are ducted to a 49,000 scfm carbon adsorption system for recovery.

The capture/control system at Plant 7 was performance tested in December, 1978 (B-1, B-2). The following measurements were made: 1) Solvent input to the system was determined by monitoring plant ink and solvent flow meters, by analyzing grab samples of ink for solvent content, and by estimating solvent contribution of the system make-up air stream; 2) Captured solvent was determined by monitoring solvent concentrations (and air flow rates) in the carbon adsorber inlet duct on a semi-continuous basis using GC and FID; 3) Recovered solvent quantity was determined from plant flow instrumentation; 4) Carbon adsorber stack solvent losses were determined on a semi-continuous basis using GC and FID; and 5) Solvent losses in the wastewater were calculated by determining wastewater flow rate and solvent concentration. Many of the measurements were made on a grab (non-integrated) basis, but details of testing period times are not reported.

The average overall efficiency as determined by comparison of recovered solvent and inlet solvent rates (liquid-phase data) is reported as 92.4 percent (range of 88-97%). The liquid-phase measurement methods are straightforward, reasonably integrated, and capable of yielding fairly accurate apparent overall efficiency data. In contrast, the overall recovery efficiency by the liquid/gas-phase method ranged from 62 to 87 percent (capture efficiency 63-89%, and control efficiency 98-99%). The data representing the capture efficiency by liquid/gas-phase comparison are obviously inaccurate. The liquid/gas comparisons around the coater and capture system and around the recovery device both indicate inaccuracies. These data suggest that up to 30 percent of the solvent entering the press was lost but that the carbon adsorber simultaneously recovered over 20 percent more solvent than the amount that entered it. Considering this contradiction, a material balance could not be closed around the entire system based on gas- and liquid-phase measurements.

Supplemental measurements, made in January, 1980, indicated that ambient gas-phase solvent contributions to the press may have been greater than realized during the 1978 testing. These greater inlet gas-phase solvent concentrations, resulting from infiltration from other areas in the plant, may have inflated the overall efficiency results by about 3 percent.

Errors in capture, control, and overall efficiency may be due to several factors, including variable air flow rates and solvent concentrations, the failure to identify and characterize all VOC flows into and out of the system, and errors introduced by the gas- and liquid-phase measurement and analytical methods, including noncontinuous analysis.

## B.2 PLANT 8

Plant 8 is also a publication rotogravure facility using carbon adsorption for solvent recovery. The 75,000 scfm system recovers a solvent formulation of lactol spirits, toluene, and xylene from the VOC stream captured from three printing presses.

The capture/control system at Plant 8 was performance tested in April, 1974 (B-1). Flow and VOC measurement/analysis methods used were similar to those used at Plant 7, except that EPA Method 25 and 25A testing were performed in addition to GC/FID analysis. The VOC sampling was conducted in a semi-continuous manner.

Based on comparisons of liquid solvent recovered and liquid solvent charged to the presses, overall efficiency for the test period averaged 84.7 percent. As with the Plant 7 data, however, the Plant 8 capture efficiencies based on liquid/gas comparisons are obviously in error. Based on the comparison of inlet liquid solvent flows and gas-phase solvent flow to the adsorber, the average capture efficiency was determined to be 59, 58, and 122 percent, respectively, for the GC/FID, Method 25A, and Method 25 analyses. Control efficiency, as determined by the adsorber inlet gas-phase VOC mass rate and the recovered liquid solvent rate, was measured to exceed 100 percent. Control efficiency, based on gas-phase analysis of inlet and outlet adsorber streams, was determined to be 94, 94, and 97 percent, respectively, for the GC/FID, Method 25A, and Method 25 analyses. Considering these contradictions, a material balance could not be closed around the entire system.

Errors introduced into the gas/liquid-phase comparisons are apparently due to largely unidentified inconsistencies in the sampling/analysis methods. Among the inconsistencies may be variable air flows and VOC concentrations and the failure to identify and properly characterize the solvent and solvent flows into or out of the system. The Method 25 results were generally very dissimilar to the GC/FID and Method 25A results.

## B.3 PLANT 10

Plant 10 operates two paper coating lines which are ducted to a single 10,000 scfm carbon adsorption system. Solvents used in the coating process include toluene, ethyl acetate, and isopropanol. Plant 10 operates with the

coater room at a slight negative pressure with respect to the outside ambient pressure. The overall effect is for all of the drying oven makeup air to come from the coater room and be pulled through the oven.

The plant routinely maintains records of solvent usage and solvent recovery, using measuremnt methods of unknown type and accuracy. During a 12-month period ending in November, 1980, overall VOC reduction efficiency averaged about 92 percent. The carbon in the adsorber beds had been in service about 5-6 years during this monitoring period.

Plant 10 was performance tested in October, 1980 (B-3). The liquid solvent rate to the coating lines was monitored in addition to carbon adsorption system exhaust VOC rate (Method 25) for a six-hour period.

The overall efficiency was assumed to be 92 percent, based on the liquid-phase data. Multiplying the overall efficiency level by the measured inlet liquid solvent mass yields the mass of recovered solvent. Totaling the recovered mass and the VOC mass measured in the carbon adsorber exhaust provides an approximation of the total VOC mass in the capture stream leading to the carbon adsorber. Utilizing the data from the inlet liquid solvent, the approximated gaseous VOC in the capture stream, and the gaseous VOC in the carbon adsorber exhaust, capture and control efficiencies of 94 and 98 percent, respectively, were determined.

No data were available for comparing results by different methods.

## B.4 PLANT 20

Capture efficiency for the print line at Plant 20, a flexible vinyl wall covering manufacturer was determined by gas- and liquid-phase measurements in September - October, 1980. The determination consisted of measuring the mass of solvent applied at the print line, the mass of gaseous VOC emissions ducted to the carbon adsorption system, the mass of gaseous VOC fugitive emissions in print room exhaust streams, and the amount of VOC retained in the coated product. VOC measurements were made on a continuous basis using EPA Method 25A at print room exhaust areas and the carbon adsorber inlet duct. Ink usage was determined by measuring changes in the level of the ink tanks supplying the print line. Ink and vinyl product samples were analyzed for solvent content. Calculated capture efficiency based on liquid/gas-phase data averaged 60.5 percent for testing conducted over 50 hours in nine days. The range of calculated capture efficiencies was from 47 to 70 percent, excluding one abnormal measurement. The efficiency results are reported to be inconclusive due to failure to close the solvent material balance, as discussed below.

A room air supply fan caused excessive turbulence around the print stations, affecting and lowering capture efficiency. Also the net flow of solvent to the printing process was difficult to accurately characterize. Finally, the mass flow of solvent through open doorways was high, due to the room air supply fan, and difficult to accurately quantify. Measurement of flows through doorways and areas other than ducting, through the use of hand-held anemometers, may be prone to greater inaccuracies, and EPA reference methods do not apply.

## B.5 PLANT 23

Efficiency testing at Plant 23, a PSTL facility, was performed in May, 1979 (B-4, B-5). The facility manufactures masking tape; a dual coater system is used to apply the release backside and the adhesive front side on continuous paper backing. The first coating oven applies the release side using a toluene/alcohol/naphtha solvent and is controlled by a thermal incinerator. The second coating oven applies the adhesive using toluene and is controlled by a carbon adsorption system. Hoods capture fugitive solvent vapors at the coating areas and are vented to the atmosphere. Solvent vapor concentrations of the air flows in and around the coating lines and control devices were measured by three methods: integrated bag samples with FID analysis, semi-continuous sampling and FID analysis, and EPA Method 25. Liquid solvent usage was determined by application rate.

The three gas-phase methods yielded different results, particularly Method 25. Furthermore, difficulty was encountered in relating the gaseous VOC flow with the liquid VOC flow. As a result, a material balance could not be completed around either the release/incinerator system nor the adhesive/carbon adsorption system. Several factors were proposed as contributing to the failure to close the material balance, including inaccuracies in flow measurements and VOC analyses.

Although a material balance could not be completed around the entire system, data characterizing the adhesive coating line and its carbon adsorption control device appear to provide a reasonable description of the performance of that portion of the system. For example, measurement of toluene rate to the coater using liquid testing methods and VOC rate in the adsorber inlet duct using EPA Methods 2 and 25 indicates a capture efficiency of 97 percent. Comparison of gas-phase determinations of VOC rates to and from the adsorber indicates a control efficiency of 88 percent, for an overall VOC reduction efficiency of 85 percent. However, these values may be distorted because they apparently do not account for miscellaneous solvent rates, e.g., the solvent that was not volatilized in the upstream release oven and therefore entered the adhesive coating operation as part of the coated product.

There were no other comparative test data to use for evaluation.

## B.6 PLANT 24

An emission test of a metal coil coating line at Plant 24 was performed in October, 1978 (B-6, B-7). Gas chromatography (GC)/FID analysis of the coating line's incinerator effluent and measurement of the solvent usage rate yielded a reported overall efficiency of 99.9 percent. The available information does not clarify how the overall efficiency was determined without measuring the total VOC mass flow to the incinerator. Detailed methods and results of the testing are not reported.

## B.7 PLANT 25

Source testing was performed at Plant 25, a metal coil coating plant, in August - September, 1979. Most of the metal coated by Plant 25 is used in the building industry for siding, roofing, gutters, awnings, and other items. Types of coatings applied include epoxy resins and primers, polyesters, acrylics, fluorocarbons, siliconized acrylics and polyesters, and polyvinyl chlorides. Solvents used in the coating process are aromatic hydrocarbons and glycol ethers. The coating line tested (one of two) is equipped with thermal incinerators for control of solvent VOC emissions.

The following VOC analyses were performed:

- total hydrocarbon (THC) sampling at the incinerator outlets,
- EPA Method 25 sampling at the incinerator inlets and outlets,
- EPA Method 25 and THC sampling at a quench zone vent, and
- EPA Method 24 analysis of coatings for solvent content.

Data representing solvent usage rate (EPA Method 24) and incinerator inlet VOC rate (EPA Method 25) indicate that process capture efficiency averaged approximately 71 percent for the test period. Corresponding control efficiency, based on incinerator inlet and outlet VOC rates (Method 25), averaged 79 percent, for an overall VOC reduction efficiency of about 56 percent. However, serious inconsistencies are reported for the EPA Method 25 and THC analyses, particularly at low VOC concentration levels. The resulting efficiency values, based on EPA Method 25 analyses, are therefore subject to error (material balance data based on THC analyses are not available). Also contributing to possible measurement error are the relatively short test periods; the above efficiency values are based on the results of 13 nominally 60-minute test periods conducted over six workdays.

## B.8 PLANT 26

The VOC system at Plant 26, a paper coating facility, was performance tested for a several-hour period in October, 1980 (B-3). The tested facility consisted of a single coating line controlled by an 18,000 scfm thermal incinerator operated at 1250°F. Gas-phase measurements at the incinerator inlet and outlet were made using EPA Method 25. Liquid-phase measurements of solvent charged to the coating applicator were made by monitoring the inlet solvent (carbon) mass rate. Capture efficiency was measured to range from 94 to 98 percent; incinerator control efficiency averaged 95-96 percent. Therefore, the overall efficiency averaged 91 to 93 percent.

## B.9 PLANT 27

VOC testing was performed at Plant 27, another paper coating facility, in October, 1980 (B-3). The plant operates two coating lines which are controlled by a single 15,000 scfm carbon adsorption system. The sequencing of the 3-bed carbon adsorption system, which recovers toluene solvent, is controlled by exhaust stack hydrocarbon analyzers. The only streams measured were the liquid solvent charged to the process and the gaseous VOC emissions in the carbon

adsorption exhaust air (Method 25). Control efficiency was estimated as 79 percent, based on these two flow determinations. This value was calculated assuming a capture efficiency of 100 percent, which appeared reasonable due to the efficient design of the VOC capture system. There was no obvious explanation for the low carbon adsorber control efficiency, but the observation was consistent with above-average solvent purchases by the plant.

B.10 PLANT 28

Plant 28 is a can coating facility which applies a single enamel coat to sheets of tin plate that are used to make three piece cans. After the coating process, the sheets are oven-dried. The oven exhaust is ducted to a 8,000 scfm thermal incinerator operating at 2200°F. The sheets are then cooled by ambient air, which is exhausted to the atmosphere.

The plant was tested in October, 1980, using Method 25 for gas-phase VOC analysis and measurement of inlet liquid solvent mass flow to the coating process (B-3). Gas-phase sampling was performed at the incinerator inlet, incinerator outlet, and cooling zone discharge ducts.

When the amount of solvent ducted to the incinerator inlet plus that in the cooling zone gas streams was compared with the amount of solvent applied at the coating applicator, the VOC capture efficiency was calculated as 221 percent. The inconsistency was initially thought to be due to plant data on the applied coating. However, all of these numbers were verified by Plant 28 as correct. No explanation for the poor material balance was determined. From the gas-phase analyses, the incinerator VOC control efficiency was calculated as 73 percent.

B.11 PLANT 29

Plant 29, another beverage can coating facility, was performance tested in October, 1980 (B-3). The plant has two coating lines with separate capture and control systems.

The first coating line had a drying oven, controlled by a 4,000 scfm thermal incinerator operating at 550°F, and a cooling zone, which was vented directly to the atmosphere. Gas-phase VOC analysis using EPA Method 25 and flow measurements were made at the incinerator inlet, incinerator outlet, and cooling zone exhaust. Solvent feed rates to the coating line were also monitored.

Capture efficiency was calculated to be greater than 100 percent and incinerator control efficiency was determined to be only 26 percent. The inconsistencies inherent in the capture efficiency value are attributed to questionable gas flow rate data and to frequent process startups and shutdowns. The low incinerator control efficiency may be partially attributed to inaccurate gas-phase flow measurements, but the low incinerator temperature may also contribute to relatively poor VOC destruction.

The second coating line consisted of a drying oven, controlled by a 7,000 scfm catalytic incinerator operating at 550°F, and a cooling zone, which was vented to the atmosphere. Solvent mass rates were determined using methods similar to those used for testing of the first coating line.

The material balance for the second line demonstrated a 74 percent VOC capture efficiency and the potential for 90 percent capture efficiency if the cooling zone air was directed to the incinerator. The VOC control efficiency of the catalytic incinerator was determined to be a relatively low 49 percent, which may be due to the low-temperature operation. Overall efficiency is calculated as 36 percent from the capture and control efficiencies with the potential for 44 percent.

B.12 PLANT 30

A base coating operation at Plant 30, a three-piece can manufacturing plant, was tested for VOC material balance quantification in October, 1979 (B-8). The base coating operation consists of the application and drying of a base coat on metal sheets. The coated sheets are dried at 400°F in the heating zones of an oven. The sheets then enter cooling zones within the oven prior to further processing. Oven exhaust air is vented to the atmosphere.

Six nominally 30-minute material balance tests were performed. For each test, solvent usage, dry coating application rate, and VOC emission rate were quantified. Solvent usage was determined based on coating rate and the manufacturer's specification for solvent content. Dry coating application rate was determined by before-coating and after-coating weighings of the metal sheets. VOC emissions from the heating and cooling zone exhausts were quantified using EPA Method 2 determinations of flow rate and FID and EPA Method 25 analyses for hydrocarbon concentration. Based on liquid solvent usage rate and the method 25-determined oven emission rate, capture efficiency for the system was estimated to range from 69 to 75 percent for five of the six tests (one of the tests indicated capture efficiency in excess of 100 percent). FID and Method 25 VOC emission data agreed within an average of 7 percent for the six tests.

The capture efficiency determinations at Plant 30 were based on a comparison of the solvent application rate and the solvent emission rate (captured emissions). The application rate was based on metered coating application and manufacturers figures for the solvent/coating ratio, and the solvent emission rate was based on EPA Method 25 and gas flow measurements. To develop a comparative basis between the solvent applied (lb. solvent) and measured solvent emitted (lb. carbon) both were converted to propane equivalents. This conversion was made since the solvent content was unknown and it was assumed that the carbon/hydrogen ratio of the solvent was likely similar to propane. The comparison based on this assumption will be somewhat in error if the solvents are not similar to propane (e.g. oxygenated compounds).

## B.13 PLANT 31

An interior spray coating operation at Plant 31, a two-piece aluminum can manufacturing plant, was tested in October, 1979, in a manner similar to that used for Plant 30 (B-9). After base and top coats are applied to the exterior surfaces of the aluminum, the cans receive 80 weight percent solvent, 20 weight percent solids interior spray coats. The cans are then cured in a gas-fired oven. Emissions from the base coat oven, the top coat printer and oven, and the interior spray coater and oven are ducted to a thermal incinerator operating at 1150°F. The referenced source test focused on VOC emissions from the interior spray coating operation, which includes a can transfer conveyor and the gas-fired oven.

Test results for four of the six nominally 30-minute tests indicated capture efficiencies ranging from 58 to 97 percent (based on solvent usage rate and EPA Method 25-determined VOC emission rate). For the remaining two tests, capture efficiency measured in excess of 100 percent, for unidentified reasons. EPA method 25 and FID results did not correlate closely on the average. The inconsistencies were attributed to organic condensation in the FID integrated bag samples, resulting in artificially lowered gas-phase concentrations.

Inaccuracies in the tests at Plant 31 may be somewhat attributable to the potential error described in the last paragraph on Plant 30. The same assumptions were followed not knowing the solvent content.

## APPENDIX B REFERENCES


B-1 Publication Rotogravure Printing - Background Information for Proposed Standards, EPA-450/3-80-031A, OAQPS, U.S. Environmental Protection Agency, Appendix C, May, 1980.

B-2 Graphic Arts Emission Test Report, Meredith/Burda, Inc., Lynchburgh, Virginia, Test 2, EMB Report No. 79-GRA-1A, OAQPS, U.S. Environmental Protection Agency, February, 1980.

B-3 Determination of Capture and Destruction Efficiencies of Selected Volatile Organic Compound Control Devices in the State of Illinois, EPA 905/2-80-005 U.S. Environmental Protection Agency, April, 1980.

B-4 Background Information Document for the Pressure Sensitive Tape and Label Surface Coating Industry, EPA-450/3-80-003A, OAQPS, U.S. Environmental Protection Agency, Appendix C, May, 1980.

B-5 Draft Pressure Sensitive Tapes and Labels Emission Test Report, OAQPS, U.S. Environmental Protection Agency, June, 1979.

B-6 Metal Coil Surface Coating - Background Information for Proposed Standards, EPA-450/3-80-0359, OAQPS, U.S. Environmental Protection Agency, October, 1980.

B-7 Industrial Surface Coating (Coil) Emission Test Report, Precoat Metals Incorporated, St. Louis, Missouri, EMB Report 79-ISC-10, OAQPS, U.S. Environmental Protection Agency, October, 1980.

B-8 Industrial Surface Coating Cans Emission Test Report, American Can, Forest Park, Georgia, EMB Report 79-ISC-7, OAQPS, U.S. Environmental Protection Agency, August, 1979.

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